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NONMETALLIC INCLUSIONS IN STEEL

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Abstract

Nonmetallic inclusions in steel have been a direct cause of great expense to the steel industry because, through our lack of knowledge regarding the effects of these inclusions, much time and money are spent in inspection and rejection of material containing them. The present paper points out the sources of inclusions in steel, methods of manufacture which seem best suited for the elimination of inclusions, and deals with some of the effects of inclusions in steel. It would appear that closer cooperation between the consumer and producer is necessary before the inclusion problem can be satisfactorily solved, and this can only be accomplished through a more thorough understanding of the entire problem. One of the first steps in the solution of this problem should be the preparation and careful examination of steels containing no inclusions.

Foreword

IT has been the speaker's good fortune to see the two sides of steel making, producer's and consumer's, from an independent position, and from this vantage point it has been possible to draw conclusions regarding nonmetallic inclusions which may be of interest, particularly during the present period of supercritical inspection.

Before entering into the subject matter, I wish to acknowledge

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This is the sixth Edward De Mille Campbell Memorial Lecture, presented by Dr. Charles H. Herty, Jr., physical chemist in charge of Metallurgical Section, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh. The lecture was presented at the Thirteenth Annual Convention of the society in Boston, September 21-25, 1931.

the most valuable assistance of my associates at the Bureau of Mines for the collection of a great deal of the data from which many of the conclusions are drawn. I am particularly grateful for the help given by G. R. Fitterer of the Bureau of Mines and C. F. Christopher of the Advisory Board staff.

Types of Inclusions Present in Steel

Inclusions Visible at 250 Diameters Magnification

There are two general types of inclusions in rolled steel in this category—"stringers" and "clouds." Stringers are composed of material which was plastic at the temperature of rolling, and liquid when the ingot was cast. In killed steel, stringers are usually silicates, sulphides, or silicate material containing dissolved sulphide. Alumina and aluminum silicate are generally observed as masses of tiny particles which give the appearance of clouds to the unaided eye and which appear as groups at 250 diameters magnification. These tiny particles are formed of inclusions which were solid at both the steel making and rolling temperature. Almost all stringers are visible at 250 diameters magnification, indicating that most of the liquid particles in the liquid steel had coalesced to some extent. These stringers may or may not show structure, depending very largely on the composition of the inclusion, the original rate of cooling, and the heating to which the steel has been subjected. For example, in a steel ingot, silicate particles high in silica are usually glassy; but on a double heat treatment, as in the case of a re-rolled product, these particles generally change to a gray amorphous material. The glassy particles, such as the manganese silicates, will be green, yellow, orange, or a combination of these colors, depending on the composition of the inclusion. On cold working, and sometimes on hot working, stringers may be broken up into chains if the inclusion material is sufficiently brittle. In other types of inclusions, stringers may be drawn out to very fine threads with no discontinuities. This would indicate that the physical properties of the slag comprising the stringer have considerable influence on the final appearance of the inclusion. The temperature-viscosity relation of the various inclusion slags is the determining factor on the physical condition of any inclusion for a given amount of hot or cold work. Aluminum or aluminum silicate particles show great tendencies to coagulate, but not to coalesce. This indicates that the inclusion was solid at steel-

making temperature and that coagulation was due either to grouping from surface tension effects, or to concentration of material during solidification of the ingot. There are many instances where this latter factor is certainly the cause for grouping, as the alumina particles may be definitely seen around the grain boundaries of the metal.

Sulphides are in solution in liquid steel, and their mode of occurrence in the solid metal depends on the manganese content and on the rate of solidification. It has been shown (1)[1] that the amounts of manganese and sulphur which may be mutually present in liquid pig iron increase rapidly with increasing temperature.

At 1475 degrees Cent. (2690 degrees Fahr.) the approximate freezing point of a 0.40 per cent carbon plain-carbon steel, the solubility product, per cent Mn times the per cent S equals 0.90 in pig iron. From data obtained in an earlier research on iron containing less than 0.05 per cent of carbon (2), the solubility product was approximately 0.50 at about 1550 degrees Cent. (2825 degrees Fahr.). It may therefore be stated positively that in a steel containing 0.70 per cent of manganese and 0.035 per cent of sulphur, all the sulphur would remain in solution until the steel began to crystallize, because the product per cent Mn times per cent S equals 0.0245. It is probably the concentration of sulphur in the liquid between crystallites that promotes the precipitation of manganese sulphide. Slow cooling would, of course, promote the concentration of sulphur because the mother liquor is not as completely trapped as in a rapidly cooled test. The rate of cooling has, therefore, a considerable effect on the type of sulphide which will appear. For example, in high manganese, high sulphur steels, a splash test will show very little manganese sulphide. On the other hand, the interior of a slowly cooled ingot will show manganese sulphide to be the predominant nonmetallic present. Although the term "manganese sulphide" is commonly used to designate the globular sulphide inclusion in cast steel and the elongated sulphide inclusion in rolled steel, the inclusion is actually an iron-manganese sulphide.

Sulphides are usually present in silicate inclusions, because the sulphides are quite soluble in silicate melts. For this reason, silicates have often been confused with sulphides because a silicate inclusion containing some sulphide will give a definite sulphur print. An ex-

[1]The numbers appearing in parentheses refer to bibliography appended to this paper.

ample of such a mistake was found in some broken transverse tensile tests which were investigated for inclusions. The manufacturer who furnished the broken tests stated that there was practically no reduction of area and that there were large plates of sulphides at the fracture, and in order to correct the defect he was attempting to prevent sulphur segregation in his ingots. The analysis of the steel showed only 0.016 per cent of sulphur and a check analysis on the tensile bar gave 0.018 per cent of sulphur. On extraction of the yellow plates at the fracture of the tensile test, it was found that the plates analyzed 65 per cent of silica and 28 per cent of manganese oxide. The plates were not analyzed for sulphur but gave a definite sulphur print. The inclusion was, therefore, a manganese silicate containing manganese sulphide.

In another case a large nonmetallic particle caused the rejection of a machined section of steel and the rejection was reported as "due to sulphide inclusions." A microscopic examination of a large inclusion showed a structure quite similar to that of a synthetic manganese silicate. The records of the heat in question showed that the heat had been killed with manganese and silicon in the ladle.

The above examples are typical of the confusion in identification of inclusions which results from sulphur printing or from the chromic acid test for sulphides.

In rimmed steels, most stringers are MnO-FeO complexes, or manganese sulphide, or combinations of the two. Occasionally a large silicate stringer will appear in a rimmed steel, and various data indicate that these silicate stringers arise either from nonmetallic matter in the charge which has not been eliminated during the refining period, or from erosion of the runner or ladle. As will be shown later, these large silicate stringers are dangerous for deep-drawing material. Alumina clouds are occasionally observed in rimmed steel, but there is usually enough iron oxide or manganese oxide present in the steel to flux out these alumina particles, unless the aluminum is added in the mold, in which case a considerable portion of the Al_2O_3 formed will be found in the ingot.

Particles Invisible at 250 Diameters Magnification

Particles invisible at 250 diameters magnification may be classed as discrete particles when they are 0.0002 mm. in diameter or larger, as colloidal dispersions when smaller, and as solid solution material,

There is abundant metallographic evidence that particles invisible at 250 diameters exist in steel. There is also some chemical evidence. As an example of this, ladle tests and material cut from forgings were obtained on an acid open-hearth heat in which the steel had been given a special deoxidizing treatment. The ladle test showed absolutely no inclusions at 250 diameters, but the forged material contained silicate particles. An analysis of the two specimens by the electrolytic method showed that the ladle test contained 0.023 per cent of SiO_2 and that the section from the forging contained 0.021 per cent of SiO_2. Because of the high-silica slag in the acid open-hearth furnace and the fact that silica is slightly soluble in liquid steel, it was evident that the ladle metal contained silica so finely dispersed that it could not be seen at 250 diameters, and that this material had coalesced in the ingot mold.

If a steel has been dead-killed with aluminum, the particles of Al_2O_3 are readily discernible at 500 diameters and difficultly so at 100 or 250 diameters. Aluminum silicates, formed when steel is deoxidized with aluminum and silicon or with aluminum-silicon alloys, form a grouping which can be seen easily with the unaided eye, but the particles themselves are quite small and it is necessary to use high magnification to study them individually.

Solid Solution Material

There are three general methods of determining whether material is present in solid solution in steel: (1) by determining whether the material diffuses through solid steel at various temperatures; (2) by metallographic evidence obtained at very high magnifications, in conjunction with chemical analyses of proved merit (the latter, by the way, up to the present time is subject to considerable dispute); and (3) by changes in physical properties of steel containing variable amounts of the constituent under consideration. Method 2 is in reality evidence rather than proof.

It is well known that oxygen as FeO is present as a solid solution in steel. The three methods of determining the solid solubility have been applied to this material as follows:

1. FeO has been shown to diffuse readily in steel.

2. Chemical analyses for FeO have shown considerable amounts to be present when there is no evidence of nonmetallic particles even at high magnifications.

3. The electrical resistivity of three samples of iron high in FeO, and with negligible amounts of other impurities, gave the following results: (3)

Sample No.	FeO Content	Resistivity, Micro-ohms per cm.^{3}
1	1.03	11.42
2	1.12	11.18
3	1.57	11.05

These data indicate that the electrical resistivity was practically constant, even with a large increase in the total FeO content of the metal, and that the resistivity is considerably higher than that which would be expected for pure iron. The change in resistivity must have been due to solid solution material which would have been equal in all three irons, and not to the total amount of iron oxide present. It would appear that the resistivity measurements on irons containing small amounts of FeO might definitely fix the solid solubility point of FeO in pure iron. The three methods of determining solid solubility all give a positive result, and therefore there must be no question that iron oxide is present in solid solution in iron. There is no direct evidence for solid solubility of MnO, but as this oxide is quite analogous to FeO we should expect some solid solubility of this oxide.

Campbell's (4) pioneer researches on the diffusion of sulphur through steel, confirmed by Arnold and McWilliam (5), indicated that the rate of diffusion was much faster than has been found by later investigators. The experimental method used by Campbell was open to some criticism but nevertheless gave definite proof that sulphur would diffuse through steel. Mahin's experiments (6) were exceedingly important contributions to the entire inclusion problem and showed how sulphur diffused into steel and also how it affected the crystallization of the steel at the point of high sulphur segregation. His results appear to be entirely in accord with the conclusions derived from the solubility product.

Researches of other investigators have indicated some solid solubility for FeS and less for MnS. Rates of diffusion for various materials in solid steel have been determined as follows (7):

Material	Rate of Diffusion, mm. per Hour
MnS	0.0029
MnS + FeS	0.0720
FeS	0.1147
FeO	0.1434
Fe_3C	5.7300

Andrew and Binnie (8) showed by experiments on the change at the A_3 point that sulphur was held in solid solution in iron-sulphur alloys when the melt was rapidly chilled, and that deposition of FeS occurred on reheating above 900 degrees Cent. (1650 degrees Fahr.). Their results on manganese-iron-sulphur alloys were indefinite but "seem to show that MnS, if it is at all soluble in solid iron, is only very slightly so."

There is no evidence of any appreciable solid solubility of SiO_2 or Al_2O_3 or of the silicates or aluminates high in these two constituents. SiO_2 must be slightly soluble in liquid steel, as evidenced by the silicon pick-up in the acid open-hearth furnace. Its solubility in solid steel is probably much too small to be measured by any direct method. On the other hand, silicates high in FeO or MnO might give some solid solubility of FeO or MnO in the steel, due to the distribution of FeO and MnO between slag and metal at elevated temperatures. The fact that the silicates high in FeO and MnO are rolled out into thin stringers without fracture of the nonmetallic particle is evidence that the particle is sufficiently fluid to allow diffusion of FeO or MnO from the inclusion into the steel or vice versa. Furthermore, the facts that silicate particles high in silica or alumina particles are not attended by ferrite banding after rolling, and that MnO-FeO stringers or silicates high in FeO and MnO do show such banding, are certain indications that the oxides must be present in solution in the steel surrounding the inclusions. We would expect inclusions which are soluble in solid steel to have a definite effect on its structure, and a consideration of this phase of the subject will be taken up later.

Source of Inclusions in Steel

This phase of the inclusion problem has been repeated so often that it will be unnecessary to go into detail here. However, from the standpoint of advance in the science of steel-making and the production of clean steel, there are some factors which should be emphasized. Inclusions in finished steel may be traced to one of three sources:

1. In all steel-making operations the liquid steel is in contact with refractory material, and many steel manufacturers feel that some of this refractory material may occasionally find its way into the steel through the scouring action in the runner of the furnace,

the ladle lining, or nozzle of the ladle. However, cases where these inclusions are present are comparatively rare.

2. Another source of inclusions is nonmetallic matter brought into the steel-making operation through the charge itself. In any steel-making operation where scrap and pig iron are charged, such nonmetallics must be introduced. Generally speaking, the amounts of these impurities are small and, if the refining operations are properly carried out, a large percentage of them should be eliminated because the steel is in contact with the slag for several hours.

There is one important point in this respect in a comparison of electric furnace and open-hearth steel. In the electric furnace the purity of the charge is of great importance because there is little or no action in the bath throughout the course of the operation. In the open-hearth furnace, on the other hand, there is ample time and agitation for nonmetallic matter to be scrubbed out of the steel into the slag. Therefore, it is not necessary for the open-hearth operator to select his charge as carefully as for the electric furnace operator. There is some evidence that nonmetallic matter tends to build up in a closed cycle in electric furnaces which use their own scrap. This has been thought to be particularly true of a nonmetallic which has not been mentioned up to this point—namely, nitrogen.

3. The third and most prolific source of nonmetallic inclusions is from the deoxidation process (9), and it is here that the steel maker's skill shows itself, and where the greatest advances in steel cleanliness and reliability may be made. In all steels made in the open-hearth furnace, and in many cases in electric furnace practice, it is necessary to eliminate carbon and other metalloids from the charge by oxidation. This oxidation is accomplished by the transfer of iron oxide from the slag into the steel and its subsequent reaction with the various metalloids. Before the steel can be poured into the ingot mold, it is necessary to eliminate part or almost all of the residual iron oxide so that the steel will be suitable for the service intended, and it is from the deoxidation of the steel that the great bulk of nonmetallic matter present in the steel is formed.

The oxidation of the steel depends on the degree of oxidation of the slag, the carbon content of the steel, and the bath temperature. An extensive investigation now in progress at the Bureau of Mines has shown that the iron oxide content of the slag is the controlling factor under operating conditions, and that the metal is generally

from 60 to 80 per cent saturated with iron oxide (with respect to the composition of the slag) at the time the heat is ready to be tapped. Obviously, the operator who controls as closely as possible the iron oxide content of the slag has a better chance of producing a metal of uniform iron oxide content when the heat is ready to be deoxidized than an operator who pays but slight attention to the slag and allows its iron oxide content to vary over a wide range.

I have in mind two plants where the two extremes can be seen. In one, slag is uppermost in the superintendent's and melters' thoughts, and in the other it receives slight consideration. In the first plant, on a series of 100 heats the iron oxide content varied from 11 to 16 per cent. In the other, on the same grade of steel, the iron oxide content of the slag varied from 14 to 32 per cent. It is quite obvious that the first plant is in a better position to produce steel which is more uniform from heat to heat than the second plant.

There are three ways of deoxidizing steel: (1) To partially deoxidize in the ladle and to complete the deoxidation in the mold; (2) to deoxidize entirely in the ladle; and (3) to deoxidize as far as possible in the furnace and to complete the deoxidation in the ladle. Most so-called "quality shops" employ the latter method. However, the first method implies as much quality as the third, provided that the customer is satisfied.

The question arises now as to the benefits of the various ways of deoxidizing the steel. In the first place, it is advisable to produce a fluid nonmetallic particle which will have an opportunity to coalesce with other particles and rise out of the steel rapidly. In the second place, it is advisable to form as few of these particles as possible so that the minimum will be left in the steel. This does not mean that the steel should not be fully deoxidized, but that the iron oxide content of the steel should be as low as possible before deoxidation. Open-hearth baths vary from 24 to 40 inches in depth. Ladles for open-hearth steel are from 10 to 14 feet deep. It is obvious, therefore, that most of the deoxidation should be done in the furnace, provided sufficient time is allowed for the nonmetallic matter to rise out of the steel into the slag. With these two statements in mind, it is easy to understand why the operator making steel to a strict cleanliness specification employs deoxidation in the furnace as the first step and final deoxidation in the ladle as a second step.

The advantage of deoxidizing in the furnace may be illustrated

by Fig. 1—an average of 30 heats on which the iron oxide content of the metal was determined by the aluminum method (10). In this case the steel had a 0.40 per cent carbon, 0.60 per cent manganese, and 0.15 per cent silicon specification. At the time the heats were ready to be tapped, the average iron oxide content of the steel was 0.230 per cent. The heats were deoxidized with two different amounts of high-silicon spiegel in the furnace, and follow-

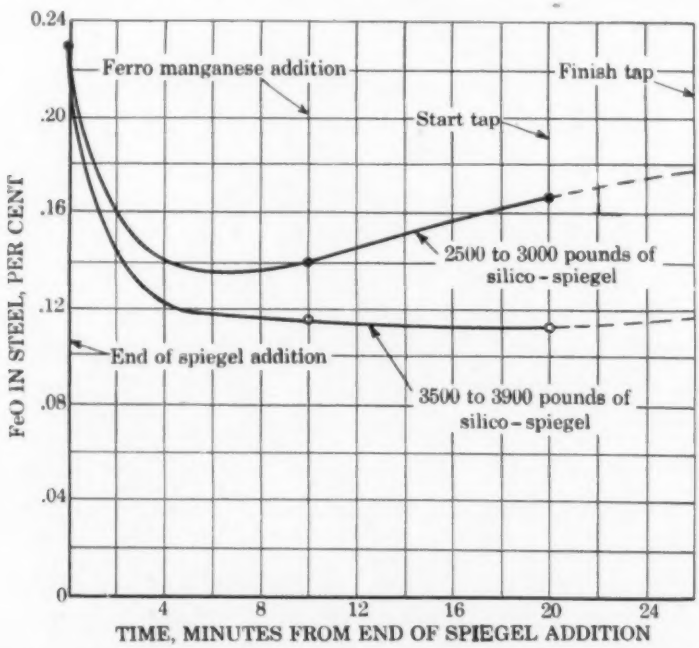

Fig. 1—Effect of Increasing Furnace Deoxidizer on FeO in the Metal.

ing this the necessary ferromanganese addition was made and ferrosilicon was added in the ladle. The heats were made in 60-ton basic open-hearth furnaces. On the first series of heats, 2500 pounds of silico-spiegel was added to the steel, the contained silicon being equivalent to 0.07 per cent of silicon in the steel. Ten minutes later ferromanganese was added, and 10 minutes later the tapping hole was opened. Just before the ferromanganese addition, the iron oxide content of the steel had dropped to 0.140 per cent. Just before the tapping hole was opened, the iron oxide content had increased to 0.166 per cent. The rise in iron oxide was due to diffusion of FeO from slag to metal which had been taking place throughout the oxidizing and deoxidizing period. An extrapolation of the curve for iron oxide showed that there was approximately 0.177 per cent FeO in the steel going into the ladle.

In the second series of heats, the amount of silico-spiegel was raised to 3500 pounds, the contained silicon being equivalent to 0.10 per cent of silicon in the steel. In this series the iron oxide content of the steel had decreased to 0.115 per cent just before the ferromanganese addition and was at 0.112 per cent at the time the tapping hole was opened. Extrapolation of this line gives 0.115 per cent FeO at the time the heat was in the ladle. The decrease in iron oxide content in this series over that in the first series was due to the extra deoxidizer added, not only decreasing the iron oxide content at the time of the addition, but also protecting the steel from reoxidation by the slag.

Now, if we assume that the silicon addition in the ladle would decrease the iron oxide content to approximately 0.03 per cent, a figure derived from the equilibrium constant for silicon and iron oxide (9),

$$K = (\text{per cent free silicon})\ (\text{per cent FeO})^2 = 1.65 \times 10^{-4},$$

the amount of iron oxide which it is necessary to eliminate in the ladle was 0.147 per cent in the case of the 2500-pound spiegel addition, and 0.085 per cent of FeO in the case of the 3500-pound spiegel addition. If the heat had been tapped without this furnace deoxidation, the amount of FeO eliminated in the ladle would have been 0.200. In terms of SiO_2 formed, the amounts would be as follows:

Deoxidizer	Per Cent SiO_2 Formed
No spiegel addition	0.084
2500 pounds spiegel	0.062
3500 pounds spiegel	0.036

It is thus seen that it is extremely desirable to deoxidize the steel as strongly as possible in the furnace before making the ladle addition.

There is a qualification which must be inserted at this point: Unless the products of deoxidation in the furnace are eliminated, there is obviously no advantage in deoxidizing there and, in fact, it is possible that more nonmetallics may be formed by improper deoxidation in the furnace followed by deoxidation in the ladle.

Another point in furnace deoxidation is that the heat should not be allowed to "open up" before tapping, because if this is allowed the iron oxide content of the steel will have increased to such an extent that the benefit of the furnace deoxidation will have been lost. It is obvious that if the heat is allowed to open up, any good effects of the furnace addition will have been nullified.

It is well known that it is more difficult to produce clean low carbon killed steel than clean high carbon killed steel. This is because it is necessary to increase the oxidation of the steel to make a low carbon heat. The FeO content of the slag is generally higher on low carbon heats and therefore the FeO content of the steel is higher. Furthermore, the rate of reoxidation of this low carbon steel is greater because of the more oxidizing slag. There are therefore more nonmetallic inclusions formed here than on higher carbon steels. It is my firm opinion that if the manganese specifications on most steels could be increased, the consumer would obtain a much cleaner product in a killed steel. The general manganese specification for low carbon steels is so low that it is difficult to get enough manganese oxide into the metal to flux properly the oxides formed from the stronger deoxidizers. It is obvious, of course, that, on account of the physical properties desired, in many grades of steel the manganese cannot be raised unless some other element is lowered. Wherever it is possible to raise the manganese specification it would seem advisable to do so.

Concentration of Inclusions and Segregation in Steel Ingots

Having discussed the various types of inclusions present in steel and having described their origins, it is proper to account for their disposition in the steel ingot. The mode of segregation of a metalloid or nonmetallic depends primarily on its solubility in liquid steel.

Killed Steel

In killed steels the crystallization of the ingot has been discussed at great length by a number of writers. One of the best and most complete discussions is by Hultgren (11) who specifies four zones of crystallization in a steel ingot, as follows: (1) Surface crystals formed by the rapid cooling of the skin of the ingot when it is in contact with the mold; (2) elongated crystals formed as the cooling rate of the steel decreases due to the formation of the air gap between the ingot mold and the ingot; (3) a still more slowly crystallized zone where the cooling rate has been retarded sufficiently so that the crystals no longer have the tendency to align themselves perpendicular to the wall of the ingot; and (4) the central zone of the ingot where free crystallization takes place.

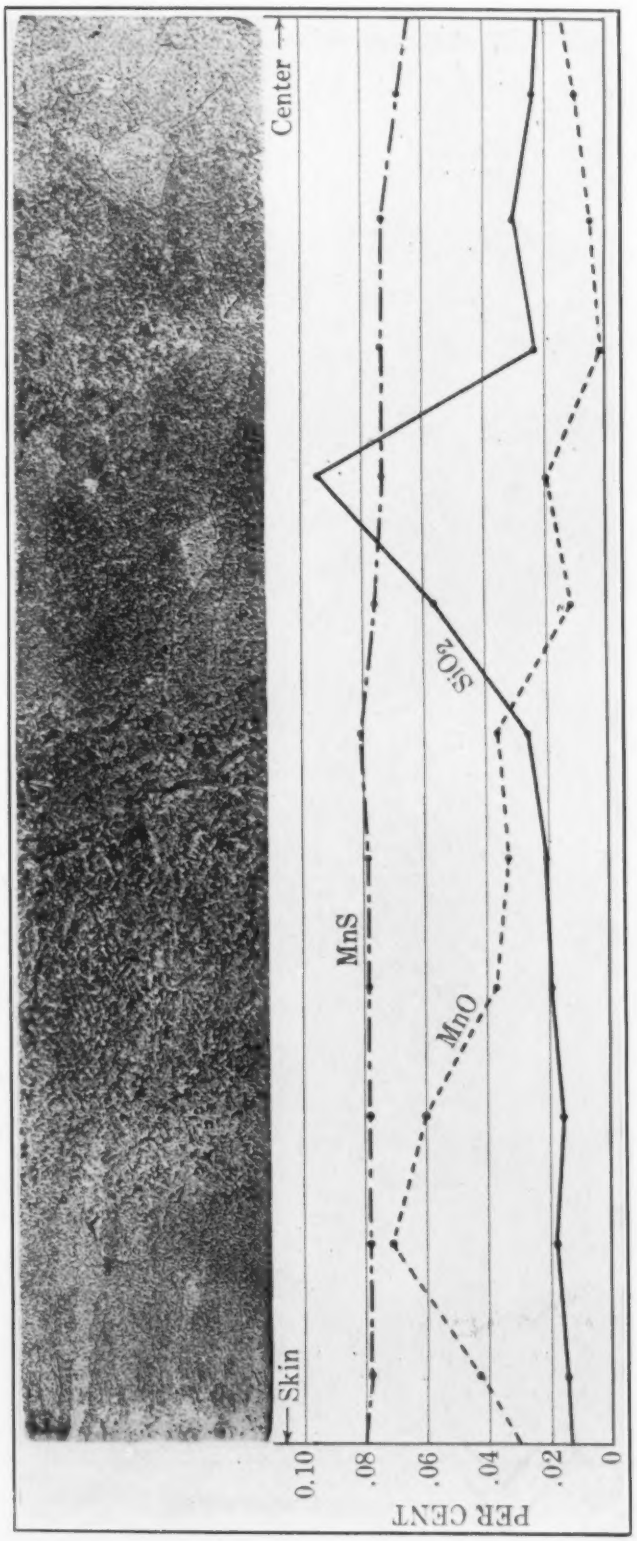

Fig. 2—Segregation of Nonmetallic Matter in Section of Ingot. Steel Deoxidized with Silico-Spiegel, Ferromanganese and Ferrosilicon.

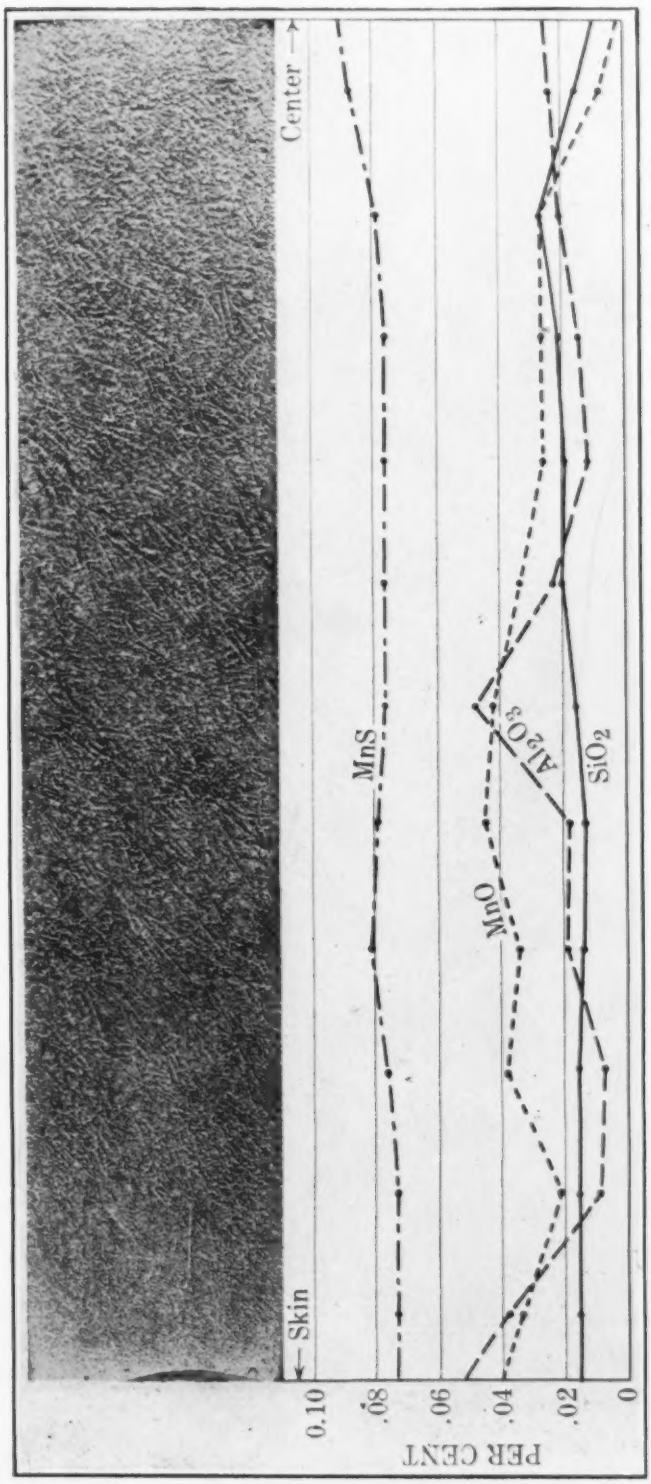

Fig. 3—Segregation of Nonmetallic Matter in Section of Ingot. Steel Deoxidized with Spiegel, Ferromanganese, Ferrosilicon and Alsifer.

Figs. 2 and 3 show electrolytically etched sections of two ingots with the segregation of nonmetallic matter plotted at the proper positions. These ingot sections were taken from the skin to the center at a point midway between the center and top of the ingots. The heat from which the ingot of Fig. 2 was cast was made by deoxidizing the steel with silico-spiegel in the furnace, followed by the ferromanganese addition in the furnace, and the deoxidation was completed by an addition of ferrosilicon in the ladle. The heat from which the ingot of Fig. 3 was cast was made by retarding the carbon elimination by a small addition of ordinary spiegel and deoxidizing in the ladle with ferromanganese, ferrosilicon, and Alsifer. The analysis of the two heats was:

	Per Cent				
	C	Mn	P	S	Si
Ingot of Fig. 2	0.36	0.52	0.018	0.027	0.19
Ingot of Fig. 3	0.38	0.48	0.012	0.028	0.17

The four zones of crystallization described by Hultgren are clearly shown in Fig. 2. The etchant brings out the crystallization to a marked degree, and there are many points of interest which could be discussed on ingot structure, secondary crystallization, and other technical details. However, we will confine ourselves to the segregation of nonmetallic matter and its connection with crystallization. The ladle test analyzed 0.023 per cent of SiO_2. Apparently the globular silicates, which are represented largely by the percentage of silica in the steel, are simply pushed forward ahead of the growing crystallites until the point of free crystallization occurred. At this point there was no reason for the silicate particles to move in any direction except upwards and, because in this particular ingot the particles were rather small and had no appreciable rising velocity, the wall of high silica content was simply held in place by the final crystallization of the center of the ingot. There being no reason for silica particles to diffuse from a region of high concentration to a region of low concentration, the center of the ingot had the same silica content as the original steel. The fact that the MnO segregation line does not follow the silica line indicates that some of the MnO in this particular ingot was not combined with silica as manganese silicate. Furthermore, the manganese oxide concentration decreases toward the center of the ingot in a manner which indicates that manganese oxide had risen out of the central zone of the ingot toward the sinkhead, so that more manganese oxide was found at the base of the sinkhead than at any other point in the ingot. It was

unfortunate in this case that the sections sampled happened to fall almost exactly in the zone of a bridge across the ingot. Just below the sections sampled there was some porosity and above the sections an increase in carbon concentration in the steel. For this reason there is little or no sulphur segregation. However, the fact that the sulphur segregation in no way followed the silica segregation is strong proof that the sulphur in the liquid steel was in solution, and was not present as globules of iron-manganese sulphides. This point has been explained in a previous section of this paper. On this ingot there was the normal segregation of phosphorus and carbon present in almost all ingots—that is, there was a slight segregation from outside to center amounting to about 0.04 per cent of carbon and 0.005 per cent of phosphorus.

In the ingot of Fig. 3 the structure is so entirely dendritic that it is almost impossible to follow the zones of crystallization. However, the alumina curve indicates a maximum at about midpoint between the center and skin of the ingot, and this is probably the point at which free crystallization commences. The addition of aluminum to the ladle brought the silica content of the steel to a considerably lower value than in the ingot of Fig. 2, substituting Al_2O_3 in its place. The maximum of silica in Fig. 2 and alumina in Fig. 3 corresponds very closely to the lines of high segregation of nonmetallics described by Dickenson (12).

It might be noted here that in the discussion of Hultgren's paper (11) Whiteley stressed the fact that sulphur segregated in the same manner as carbon and phosphorus, particularly in the top of the ingot, and he stated that this was true in spite of the fact that sulphide of manganese and iron appears to be insoluble and to be dispersed in the liquid as minute globules. The above information on segregation, combined with the solubility product given previously, shows that the idea that sulphides are insoluble in liquid steel is quite erroneous, and that they simply precipitate out during the crystallization of the steel.

At the time of writing, the analyses had not been completed on all the ingots of the series under investigation, but the results so far obtained show quite definitely that there is a wide variation of nonmetallic content at various points in the steel ingot. These variations are not due to analytical error, as shown by the trends of consecutive analyses. This variation in nonmetallic content in a steel ingot cannot be stressed too highly, as inspection of finished material is too often based on metallographic evidence from an extremely limited

quantity of steel. As a matter of fact, there is no doubt that there are rejections based on dirty steel because the sample has been taken at a peak of segregation and acceptance where a sample has been taken at a point of minimum nonmetallic content. Any number of cases could be cited where the minimum point of segregation in a very dirty ingot is lower in nonmetallic matter than the maximum point in segregation of a very clean ingot. The utmost importance should therefore be attached by the consumer to the proper sampling of the steel.

Rimmed Steel

Rimming steel, used in large amounts for sheets, strip, etc., is generally partially deoxidized with ferromanganese, followed by a small addition of aluminum in the ladle or the mold to control the evolution of gas from the ingot. The major nonmetallics in this grade of steel are MnO-FeO complexes, sulphides, and small amounts of SiO_2 and Al_2O_3. The amount of MnO formed on deoxidation depends on the oxidation of the bath before deoxidation, the temperature, and the amount of manganese added. The FeO-MnO diagram (13) indicates that FeO-MnO slags formed on the deoxidation of rimmed steel should almost always be liquid, but there are some cases in which this may not be altogether true, particularly if the steel is too low in iron oxide before the ferromanganese addition. If the operator can obtain the proper rimming action in the mold, this grade of steel will usually be quite free from oxide inclusions, but may contain large amounts of sulphides in the upper central sections of the ingot due to normal sulphur segregation. Most of the oxygen present in this grade of steel is in solid solution. There is only one way to prevent sulphur segregation in rimming steel, and that is to have no sulphur in the ladle metal. The sulphur content of this low carbon steel is quite important in some grades of deep drawing steels. Silicate inclusions, if present, are due to refractories or to an unusually dirty charge.

In an ingot of rimmed or partially deoxidized steel the skin of the ingot is extremely low in metalloids and there is a high concentration of metalloids in the upper central section of the ingot. As this type of steel crystallizes, there is a brisk evolution of gas from the solidifying surfaces which carries away rapidly the mother liquor present in the surface of the crystals. This is in direct contrast to crystallization in killed steels, where the mother liquor is trapped be-

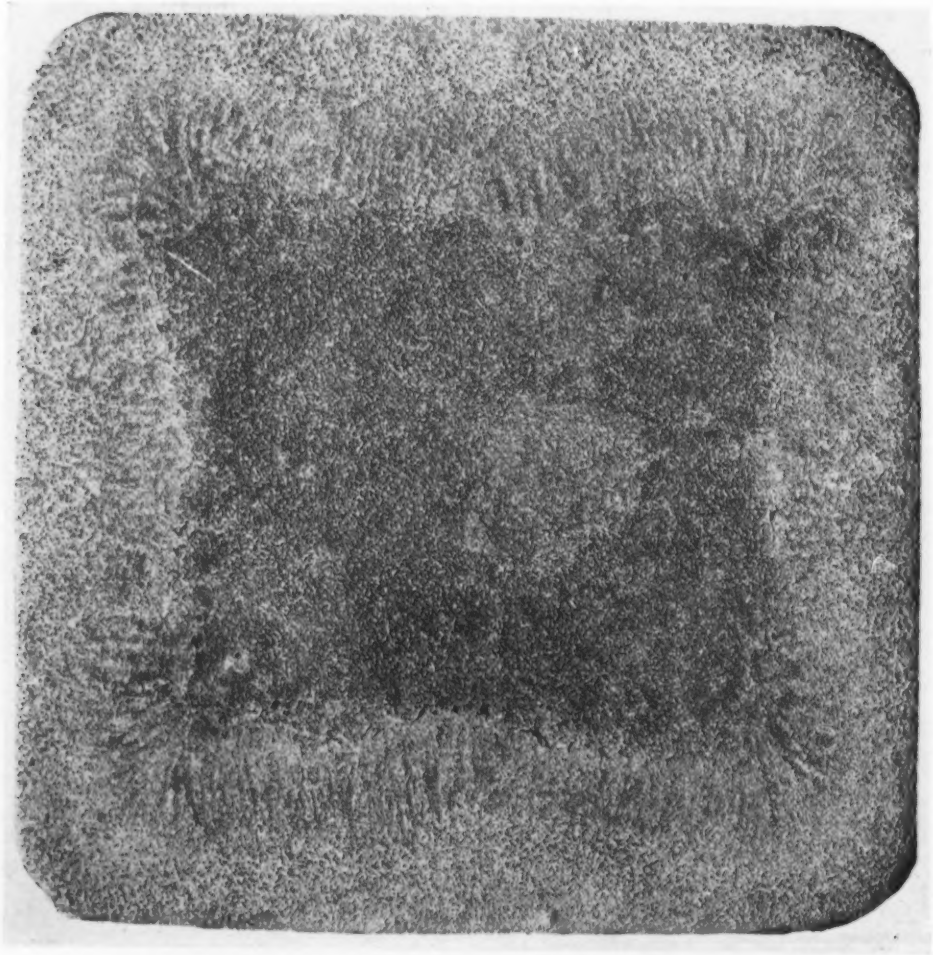

Fig. 4—Cross Section of Rimmed Steel Billet. Electrolytic Etch. Actual Size.

tween the growing crystals and the skin of the ingot varies but slightly in composition from the ladle test. In a rimmed steel this removal of enriched mother liquor continues until free crystallization takes place. At this time the steel has become viscous due to the drop in temperature and the gas bubbles cannot escape so easily. This causes a zone of blowholes in rimming steel, at which point there is an increase in metalloid content of the steel. This increase continues until the center of the ingot is reached, where maximum segregation is found. Fig. 4 shows an electrolytic etch of a cross section of a rimmed steel billet. The line of blowholes at the change of crystallization is plainly seen.

Considerable nonmetallic matter in rimmed steel is brought to the surface of the steel by the brisk convection currents at the crystal sur-

faces, and a scum high in manganese oxide and iron oxide is always found on the top of a rimmed ingot. If the rimming action is accentuated by mechanical agitation, the amount of MnO and FeO eliminated from the ingot is increased a great deal. It sometimes happens that, due to a sluggish rimming action or to an excessive amount of nonmetallic matter in the steel, a considerable amount of this nonmetallic matter is trapped in the blowhole zone which is formed when free crystallization sets in. When this occurs, the steel is apt to be of poor quality because there will be a large number of individual particles which coalesce into one large particle in the blowhole and give rise to long stringers of silicate material or of MnO-FeO complexes. Furthermore, gas bubbles, which cannot be completely removed on account of the high viscosity of the steel, are apt to result in segregated streaks in the rolled steel. Hultgren (11) has postulated a gas bubble rising through a liquid containing suspended crystals which are pushed aside by the passage of the bubble and adhere to one another so that only the mother liquor flows back into the path taken by the gas bubble. This would account for streaks of carbon segregation in this grade of steel but not for streaks of ferrite banding.

The extremely high sulphur segregation occurring at the same point as carbon and phosphorus segregation, and the fact that sulphur does not appear to segregate at the blowhole zone, are other indications that sulphides are soluble in liquid steel. Little experimental work has been done on segregation of FeO in rimmed steels, but the work done indicates a high concentration of FeO in the center of the ingot at the same point where carbon, phosphorus, and sulphur segregation are observed. Grossmann (14) gives the oxygen content of a rimming steel as follows: rim —0.019 per cent of oxygen (0.085 per cent FeO); core—0.067 per cent of oxygen (0.30 per cent FeO).

From the preceding discussion on killed and rimmed steel segregation, it may be inferred that, although the segregation of oxides and sulphides may be modified somewhat by the method of crystallization and the type of the ingot, there are only two possible ways to prevent such segregation: (1) to cast the steel into such small ingots that the entire mass solidifies almost instantaneously; and (2) to produce a steel essentially free from suspended nonmetallic particles and extraordinarily low in sulphur.

The difficulty of preventing segregation in small ingots has been demonstrated (15), (16) in steels made dirty intentionally by the

addition of silicon and cast immediately into 3-inch molds. A high segregation of silica occurred in spite of the rapid cooling of the small ingot.

Effects of Inclusions in Steel

It is an old axiom that the more we learn the less we know. A superficial survey of inclusions in steel generally ends in the conclusion that there are present in the steel a considerable number of particles which are of a different composition from the iron-carbon alloy itself and which must affect the physical properties in various degrees. The more deeply the inclusion problem is studied, however, the more convincing becomes the thought that this is a most complex problem. It involves steels in a multitude of conditions due to the unusually large number of combinations of chemical composition which are given a wide variety of heat treatments. Therefore, the physical properties of the base metal vary widely depending on the service for which the material is to be used. Add to these almost innumerable conditions two other variables—the size of the nonmetallic particle and the distribution of these particles in steel, and we have a subject which is extremely involved.

A difficulty which presents itself immediately in looking at this problem is that we have little knowledge of the properties of the base metal. It is almost impossible to find any reliable data on pure alloys of iron, carbon, and manganese, for example. The data on commercial plain carbon steels are, of course, voluminous, but these data include many variables in addition to the predominant components iron, carbon, and manganese. Therefore we have little indication as to the possibilities of varying the physical properties by purifying the metal on a commercial scale. Furthermore, there are few data on steels in which nonmetallic inclusions are present in the maximum amounts possible. Consequently, we have little knowledge as to the limits within which commercial steel is made, and it would appear at the outset that one of the most important contributions which could be made to steel manufacturers and consumers is to determine whether steels are capable of being improved considerably in physical properties or of simply being made more uniform.

In order to make a comprehensive statement regarding inclusions in steel, it is necessary to go into detail on each and every product and every steel which goes into such a product. This obviously requires a tremendous amount of experimental and investigational

work. It would seem logical to begin with a study of the fundamental properties of steels, and with this firm foundation to carry our studies into and beyond present day steel-making methods. This paper will not attempt a survey of such an investigation, but will present some evidence regarding inclusions as far as our present experimental methods and results warrant.

Inclusions Visible at 250 Diameters Magnification

Steels Used for Deep Drawing Operations

The steels used for deep drawing operations are usually made from a rimmed steel ingot. As has been shown previously, most of the nonmetallic matter in this grade of steel is solid solution material, but, as indicated previously, there are cases where large inclusions are present. A typical failure in a deep drawing material is the rupture of the steel at some stage of the drawing operation. Figs. 5 and 6 show the cross section of a sheet which failed on such an operation. Examination of the sheet showed a major cavity which extended into the narrow crack longitudinally in the piece. The large cavity contained a gray inclusion, and by actual measurement this cavity was found to correspond to the position of the secondary blowholes in a rimmed ingot. The first evidence was, therefore, that in some manner nonmetallic matter had segregated in these blowholes, had elongated on the hot and cold working of the steel, and on deep drawing the steel had failed at this point and the rupture had proceeded along the line of the blowhole zone. A narrow strip was cut from each of two such pieces along the direction of the failure, and corresponding strips in adjacent sound steel. Each strip was analyzed by the electrolytic method, with results as follows:

Sample	Strip	SiO_2	Per cent MnO + MnS
A	Ruptured	0.016	0.043
A	Sound	0.006	0.044
B	Ruptured	0.017	0.050
B	Sound	0.007	0.042

Here is abundant evidence that the failure was due to a large streak of silicate material which had been trapped in the blowholes. From the same ingots, strips were deep drawn successfully, even though they contained some short fine stringers. It was evident, therefore, that in this type of operation there was a critical size of nonmetallic particle above which failure would result, and below which the steel would draw well.

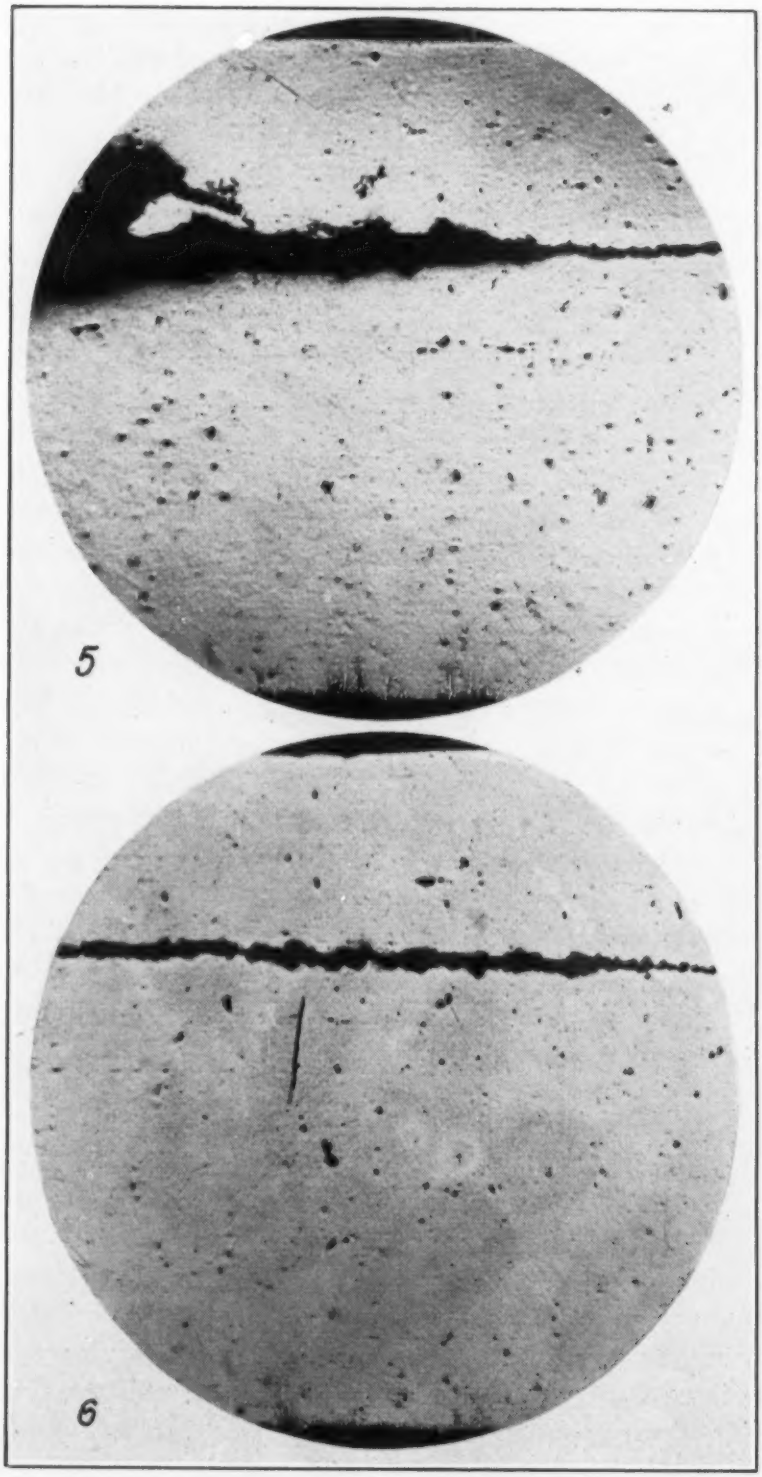

Fig. 5—Internal Tear on Deep Drawing. Low Carbon Steel Sheet. × 100.

Fig. 6—Internal Tear on Deep Drawing. Same Material as Fig. 5 Showing a Different Section. × 100.

Another type of defect in deep drawing material is the apparent recrystallization of the metal on severe cold working. Such a defect is probably connected with the normal action of the iron-carbon-manganese alloy under these conditions. It is possible, however, that this condition of recrystallization might be accentuated by solid solution material.

Piercing Operations

In certain seamless tube piercing operations it is generally true that steel which is extremely dirty at the center of the ingot fails at the point of concentration of impurities. Fig. 7 shows the ruptured section of the inside wall of a seamless tube. Fig. 8 is an enlarged section of A, Fig. 7, and shows the typical dark-gray silicate inclusion. In Fig. 7 the rupture can be seen extending from the open tear directly to the inclusion marked A. On other tubes from this heat, welts were observed on the inside surface of the tube wherever a large nonmetallic inclusion was found just below the surface of the steel. Metallographic examination indicated that the inclusion was high in silica. On heats which contained small silicate inclusions, no tendency for the steel to rupture was noted. Furthermore, large inclusions which were located more deeply in the steel had no effect on the inner surface. This is evidence that a limiting size of particle exists for this particular type of work. The action in this case was a violent torsional stress on the inner wall of the tube.

In another sample of seamless tube where large inclusions were plentiful at the center of the billet, the steel analyzed 0.071 per cent of SiO_2 and 0.058 per cent of MnO + MnS. Here again the silica was predominant, and a large percentage of this heat was rejected for badly torn inner walls of the tubes. In both the latter examples, the presence of an extra 0.10 to 0.20 per cent of manganese in the steel might have resulted in the formation of sufficient MnO to allow these high silica particles to be fluxed out before the steel was poured into the ingot molds.

A further examination of tube steel made under different conditions substantiated the observation that numerous small inclusions had little effect on the inner surface, but that large inclusions had a pronounced effect. The decrease in size of inclusions may be obtained either by producing deoxidation in such a way that the inclusions originally formed are large enough to escape from the metal before solidification, or by adding sufficient aluminum to deoxidize

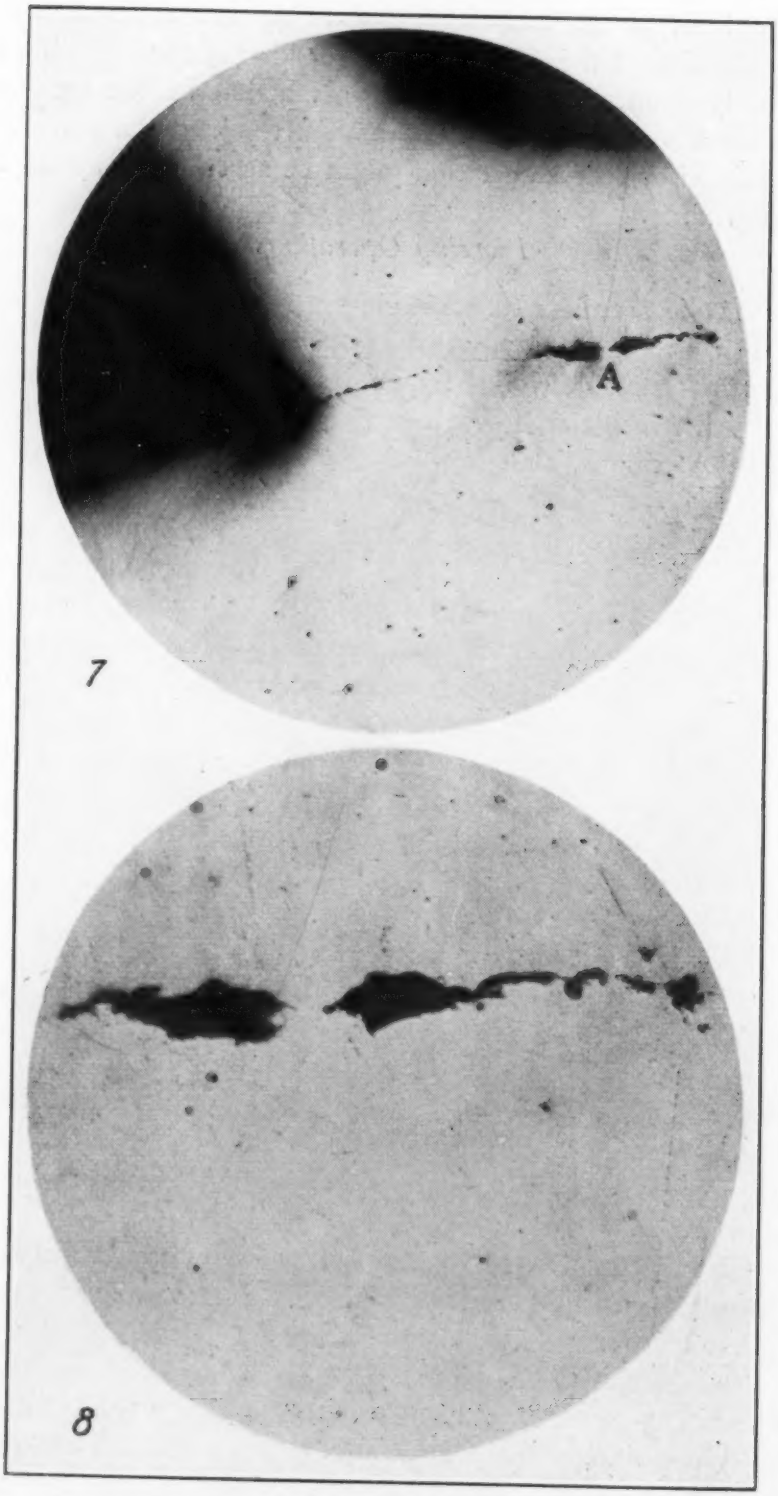

Fig. 7—Rupture in Internal Wall of Seamless Tube, Due to Large Inclusion. × 100.
Fig. 8—Enlarged Section of A in Fig. 7. × 300.

manganese silicate inclusions already present so that the steel contains only small inclusions composed largely of silica and alumina.

Seams

External seams.—External seams in killed steel are the result either of minute blowholes in the skin of the ingot, or of cracking of the steel in rolling. Surface blowholes in killed steel may be largely avoided by increasing the amount of deoxidizer. However, more deoxidizer results in a denser steel, and therefore for a given rolling temperature it cracks more in rolling and produces a greater number of seams. Seams resulting from cracking of the steel because of increased density may be largely eliminated by increasing the rolling temperature, making the steel more plastic. This is a point which should be kept in mind in rolling various grades of steel—namely, steels of different densities should be rolled at different temperatures if the same results, as far as surface is concerned, are to be expected.

In rimming steel, external seams are generally due to the surface blowholes which are always present in this grade of steel. The operator who makes the best quality of rimming steel controls his open-hearth furnace so that the surface blowholes are pushed well into the steel on solidification, and that there is a heavy skin of metal between the actual surface of the steel and the outside line of blowholes. It is at this point that the skill of the open-hearth melter is evidenced in rimming steel practice. If the blowholes are too near the surface they are exposed when the ingot is scaled in the soaking pit, and external seams are inevitable.

Internal seams.—A great deal of stress has been placed on internal seams during the past few years due to the physical specifications set with respect to bend testing, upset testing, and the severe conditions imposed because of the increased speed of machinery in the cases of bearing surfaces. It appears that in many cases large internal seams will certainly cause difficulty under severe service conditions. Here again there is unquestionably a point at which size of seam is critical, but this critical seam size has never been defined by published experimental work. From the standpoint of the consumer and the manufacturer it would seem highly desirable to design a test to cover this point.

Internal seams are of two types—sulphide seams, or oxide seams. Sulphide seams are usually associated with ghost lines, but

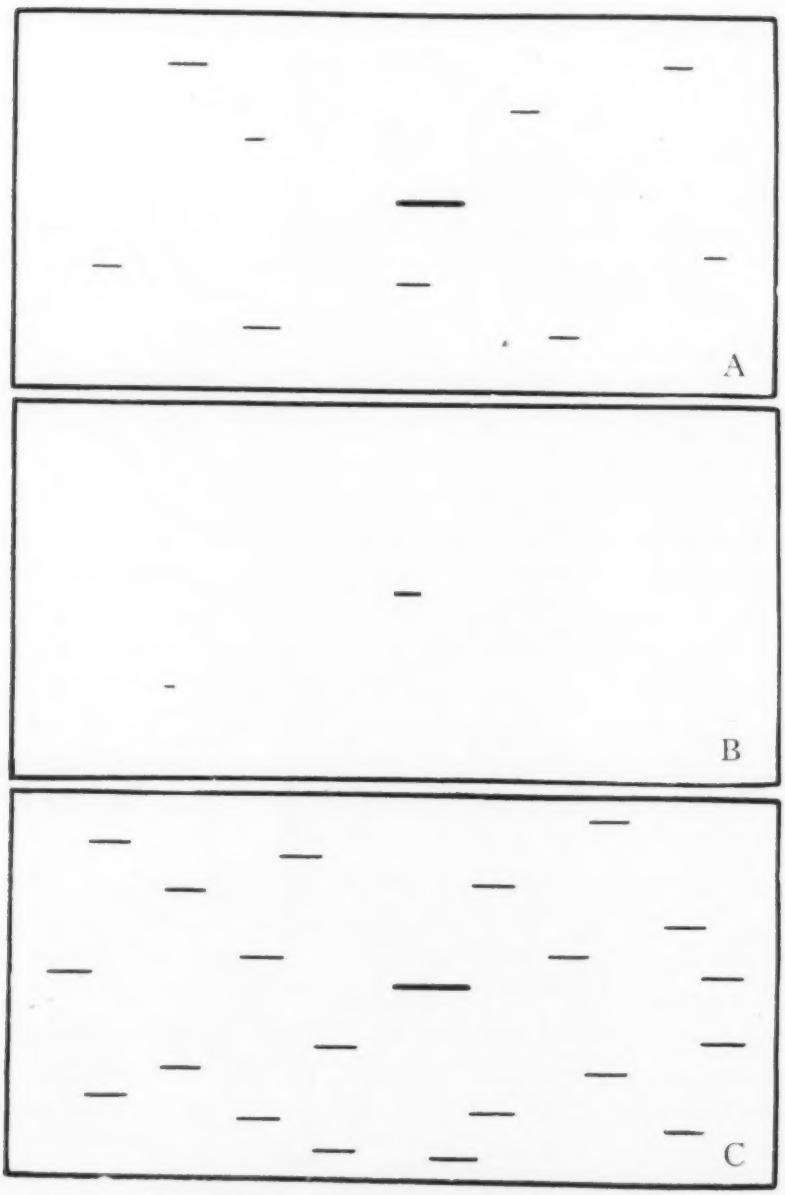

Fig. 9—Seam Inspection, Step-down Tests. Drawing Depicting the Relation of Internal Seams to Method of Deoxidation. Lines in each rectangle represent actual number and length of average number of seams in all step-down tests from heats made according to practices noted in text. The heavy line in center of each rectangle is average of longest seam in each step-down test.

oxide seams may be present in steels entirely free from this latter defect. Internal seams are due solely to the method of steel making. An excellent example of the way in which steel-making practice governs the number of seams in step-down tests is shown in Fig. 9. This represents three practices of making steel, each rectangle rep-

resenting the area of the step-down test, some 400 square inches of steel, and the lines in each rectangle the actual number and length of the average number of seams in all step-down tests from the heats made. The heavy line in the center of the rectangle is the average of the longest seam in each step-down test. A of Fig. 9 represents heats made by deoxidizing with 2500 to 3000 pounds of silico-spiegel, followed by a furnace addition of ferromanganese and an addition of ferrosilicon in the ladle. B of Fig. 9 represents the same grade of steel, the amount of silico-spiegel being increased to 3500 pounds. These heats are the same as shown in Fig. 1, in which the elimination of FeO in the furnace is shown to have increased greatly with an increased amount of deoxidizer. The additional FeO eliminated from the steel by the addition of the extra silico-spiegel resulted in a marked decrease in the number and length of internal seams. C of Fig. 9 represents the step-down test from heats in which a smaller amount of ferrosilicon was added in the ladle than to the heats of A. On these heats ghost lines were plainly visible, and the number of seams reported increased tremendously. The increase in seams here is due not only to silicates, but also to sulphides, the sulphides segregating to a much greater extent on this steel than on the steels represented in A and B.

Fig. 10 shows an electrolytic etch of a section of a steel containing 0.40 per cent carbon, 0.50 per cent manganese, 0.08 per cent silicon. This heat contained numerous ghost lines and seams. The electrolytic etch shows that in many of the ghost lines there were no signs of seams. A few seams occurred exactly in the center of the ghost line, but in most cases seams were apparent where there were no ghost lines. In this type of steel the silicates tend to segregate with the sulphur to some extent. In a more fully killed steel the sulphur and silicate segregation does not occur at the same point. Figs. 11 and 12 are photographs taken on a silicate seam. Fig. 11 is unetched; Fig. 12 is etched with picric acid. Figs. 13 and 14 show an internal seam in a heat treated with aluminum-silicon alloy. Fig. 13 is unetched; Fig. 14 is etched in picric acid. Alumina streaks resulted in a tearing of the metal at one point, but there was no evidence of banding or ferrite segregation around these inclusions. Figs. 15 and 16 are taken on a ghost line in which a seam was reported. Fig. 15 is unetched; Fig. 16 is etched with picric acid. There is no evidence of silicate inclusions in this seam, but there was a marked segregation of sulphides with a corresponding segregation of ferrite. Fig. 17

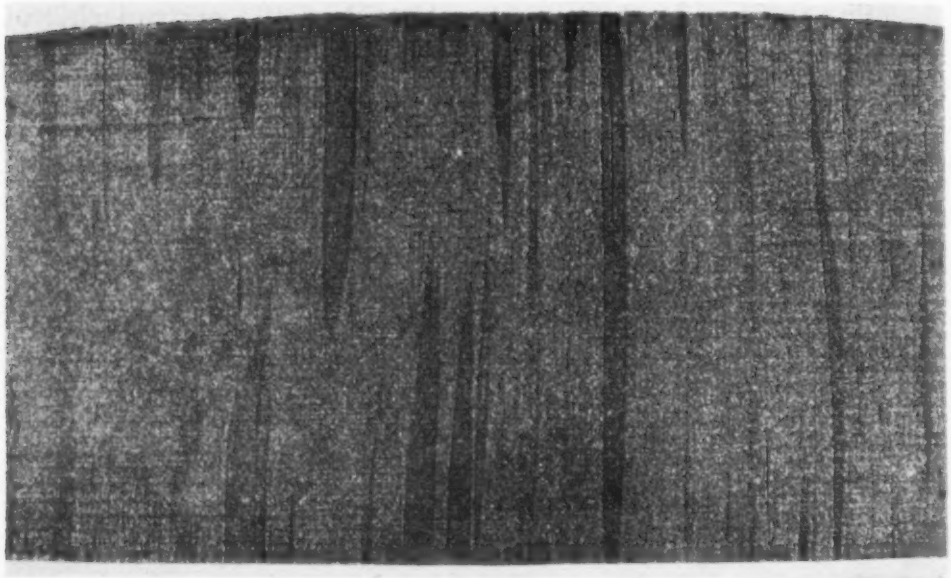

Fig. 10—Ghost Lines in 0.40 per cent Carbon Shaft. Electrolytic Etch. Actual Size.

shows another sulphide seam in which the sulphides were much smaller than in Figs. 15 and 16. In this case there is again a marked segregation of ferrite around the sulphide particles.

These data, and others which are too numerous to mention, indicate that internal seams are due to improper deoxidation of the steel. Even though it be admitted that sulphides cause seams, the fact remains that with proper deoxidation these sulphides may be scattered so as to prevent their grouping in such a way as to form a seam. In this type of defect the inclusion causing the difficulty is again a large inclusion, or a grouping of small inclusions.

Impact and Tensile Tests

Data obtained on tensile and impact testing in an investigation now in progress indicate that the physical properties of normally dirty steels do not vary to any marked degree with the total amount of inclusions present. The size of the inclusion appears to be of much more importance than the total amount of inclusions. For example, consider three steels of the following analysis: 0.17 per cent carbon, 0.65 per cent manganese. Steel No. 1 was made in a commercial open-hearth furnace at a plant producing quality steel. Steels No. 2 and 3 were made in the electric furnace laboratory of the Bureau of Mines. The deoxidizing treatment on these two steels was as follows: The heat was melted at about 1 per cent of carbon and

ored down to 0.15 per cent carbon. At this time the slag anlaysis was quite similar to that of a large open-hearth furnace making this grade of steel. Twenty-pound ladles of the metal were withdrawn, the deoxidizers were added in the ladle, and the metal was immediately poured into 3-inch ingots. These 3-inch ingots were forged to 1¼-inch square bars. Steel No. 2 was deoxidized in the ladle with ferro-silicon and ferromanganese. Steel No. 3 was deoxidized with aluminum and ferromanganese, the silicon addition and the aluminum addition being made to give the same percentage of these two elements in each ingot. Impact tests of the normalized steel showed that the commercial steel A had an impact value of 81 foot-pounds (Izod square-notched bar). Steel B gave an impact value of 65 foot-pounds and steel C, 82 foot-pounds. Steel A was a commercially clean steel. Steel B contained 0.17 per cent of SiO_2, and steel C, 0.200 per cent of Al_2O_3, both these figures indicating extremely dirty steel. In steel B the inclusions were large silicate stringers, and in steel C were fine clouds of alumina particles. It is quite evident in this case that the predominating factor in impact strength was the size of the nonmetallic particle. Apparently the fine particles of alumina had no effect on the impact strength, whereas the large silica particles decreased the impact strength considerably. Unfortunately, at this time other physical properties have not been determined on these steels. In general, however, both on tensile and impact strength after normalizing, the total amount of nonmetallic matter does not appear to have much effect, but the size and distribution appear to be factors of some importance.

An important exception should be noted at this point. In an investigation in progress on an acid open-hearth alloy steel, a decided rise in tensile and impact strength was noted when the open-hearth practice was changed and a marked increase in cleanliness of the steel accompanied this change. A comparison of the physical properties and cleanliness of these steels is given below:

Open-hearth practice	Ultimate strength, lbs. per sq. inch	Elastic limit, lbs. per sq. inch	Elongation in 2 inches, per cent	Reduction of area, per cent	Izod impact value ft.-lbs. per sq. in.	Per cent SiO_2 in steel (electrolytic method)
A	121,500	110,900	14.4	24.1	18.0	0.026
B	127,000	114,500	16.3	30.9	28.0	0.019

These results, with those given for dirtier steels, would indicate that up to a certain point in cleanliness inclusion size is important, whereas beyond that point the total amount of inclusions becomes a factor.

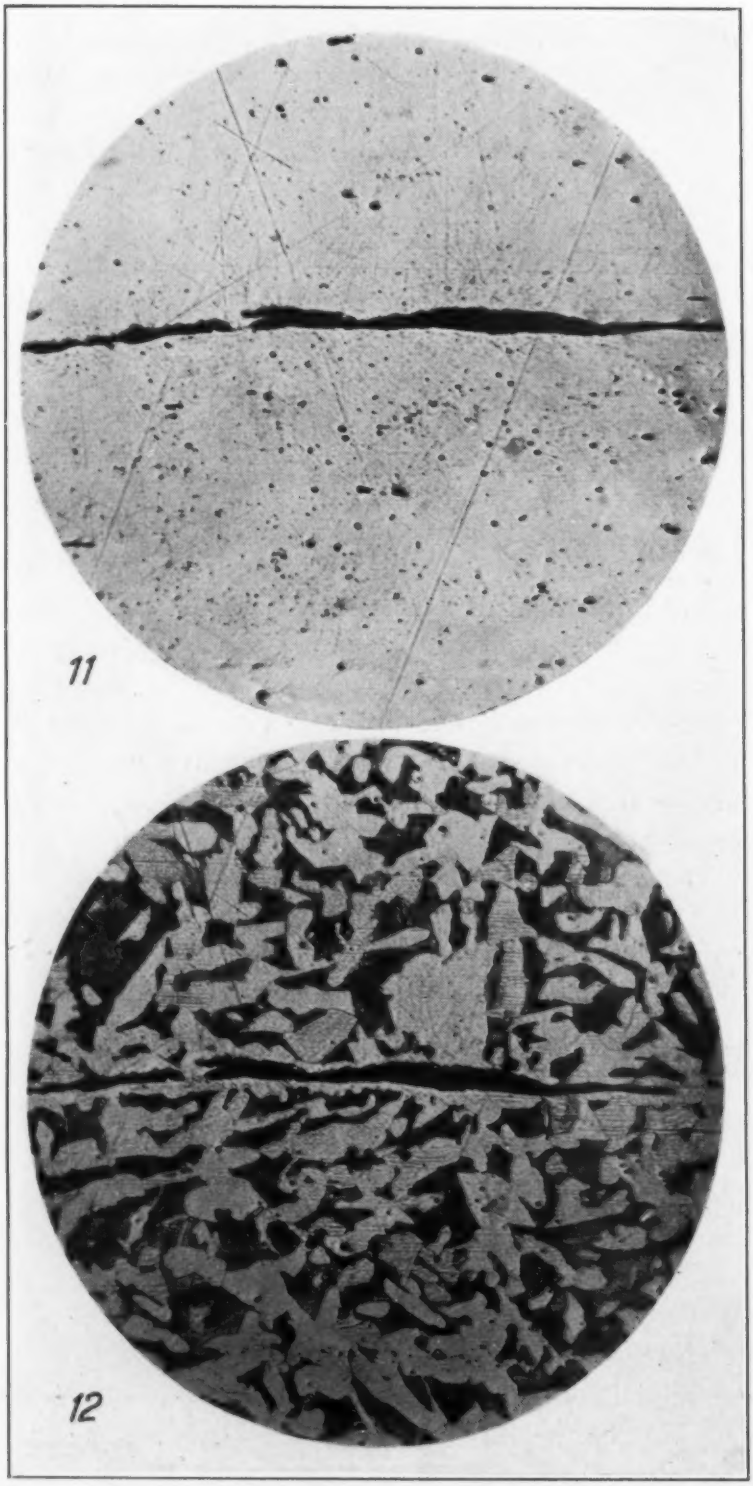

Fig. 11—Silicate Seam in 0.40 per cent Carbon Steel. Unetched. × 100.

Fig. 12—Same Section as Fig. 11. Etched with Picric Acid. × 100.

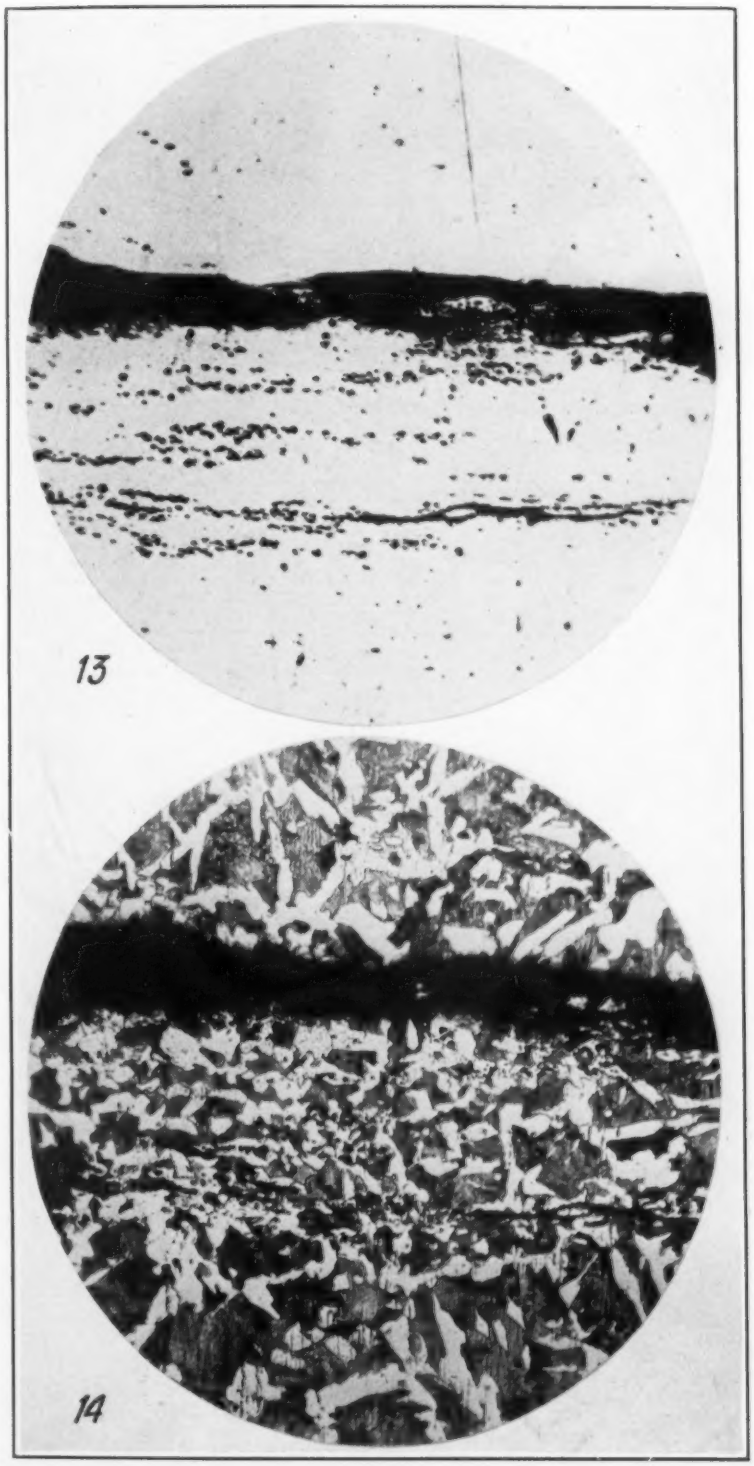

Fig. 13—Rupture and Seam in Aluminum Silicate Streak in 0.40 per cent Carbon Steel. Unetched. × 100.
Fig. 14—Same Section as Fig. 13. Etched with Picric Acid. × 100.

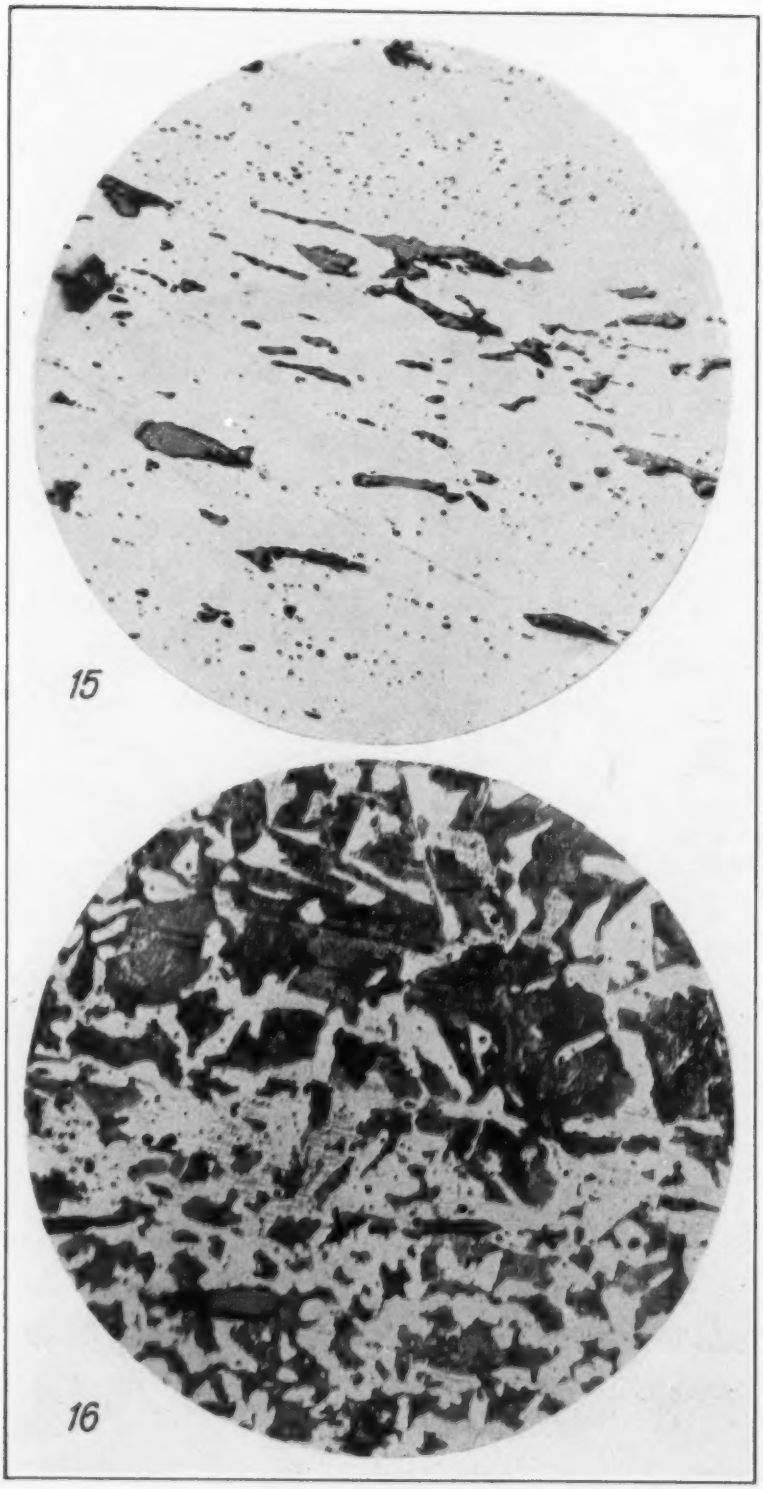

Fig. 15—Concentration of Sulphides in Seam in 0.40 per cent Carbon Steel. Unetched. × 100.
Fig. 16—Same Section as Fig. 15. Etched with Picric Acid. × 100.

In this investigation a large number of commercial steels and laboratory steels which intentionally were made dirty are being investigated, and it is hoped that the results may be of help in evaluating the effect of inclusions in steel. Here again determination of the physical properties of steels containing neither sulphides nor oxides is important because at present there is no base line on which to judge the performance of a given steel.

Fatigue Strength

It has been the general impression of investigators in this field that inclusions do not necessarily lower the fatigue limit of a given steel, but that a dirty steel will give variable results and a clean steel uniform results on fatigue testing. The small amount of work which has been done in our organization on this phase is in thorough agreement with these conclusions.

Corrosion Resistance

There has been some speculation as to the effect of inclusions on the corrosion resistance of commercial steels. A series of commercial steels were tested under the same conditions of submersion as laboratory steels in which the maximum amount of oxides as solid solution material and oxides visible under the microscope were formed (17). All these steels showed almost identical corrosion resistance under the same condition of testing. There is, of course, a great deal of question as to the reliability of laboratory corrosion tests, but in any event steels ranging from clean to extraordinarily dirty showed the same corrosion resistance in this type of test, and it may therefore be safely concluded that nonmetallic matter in steel has no effect on corrosion resistance of the material under the test conditions.

Sub-Microscopic and Solid Solution Materials

In dealing with sub-microscopic and solid solution materials, we are immediately faced with the difficulty of differentiating between the two classes. The available methods of differentiating have been discussed earlier in this paper. Experimental work (3), (18) has shown that FeO is soluble in liquid and solid steel. It is well known that sulphur is quite soluble in liquid steel and less soluble in solid steel. Although we have no direct experimental evidence on the solubility of MnO or SiO_2, we know that these two materials must

be present in solution in liquid steel to a limited extent. The fact that the reactions

$$Mn + FeO \rightleftarrows MnO + Fe \quad (1)$$

and

$$Si + 2FeO \rightleftarrows SiO_2 + 2Fe \quad (2)$$

are both reversible, that in the basic open-hearth the amount of residual manganese may be calculated from a consideration of the equilibrium of reaction (1), and in the acid open-hearth that the residual silicon may vary according to concentration and temperature changes in the system, prove that these two oxides must be soluble to some extent in liquid steel and therefore to a more limited extent in solid steel. When steel solidifies, a great deal of the soluble material is thrown out of solution, but some portion remains in solid solution.

The Structure of Steel

The effect of material present in solid solution appears to be most pronounced in the structures obtained in iron alloys after various heat treatments, and probably involves not only a change in the iron-carbon diagram, but also a change in the rate at which transformations occur, and in the diffusion of carbon through the metal. The immense amount of experimental work on abnormal steel has focused attention on this phase of the inclusion problem during the past few years. Grossmann (14), whose Campbell lecture of a year ago will be long remembered and much discussed, brought out clearly the effect of dissolved oxygen on carburized structures, attributing abnormality or normality to a tremendous change in the diffusion rate of carbon through steel below the critical point. This change in diffusion was thought to be due to the presence of dissolved oxygen. The presence of manganese in amounts above 0.30 per cent apparently prevented the absorption of oxygen during carburizing and thus slowed down the rate of carbon diffusion, a normal structure resulting. Just why manganese should prevent the absorption of oxygen whereas silicon and aluminum do not is not at all clear, and this anomaly would seem to necessitate other experiments in this field.

Grossmann reported oxygen contents as high as 0.085 per cent in 0.15 per cent carbon, 0.23 per cent manganese, 0.11 per cent silicon steel. It is extremely difficult to visualize this much oxygen in solid solution, particularly in the presense of 0.15 per cent of carbon. In the open-hearth furnace under the most severe oxidizing conditions,

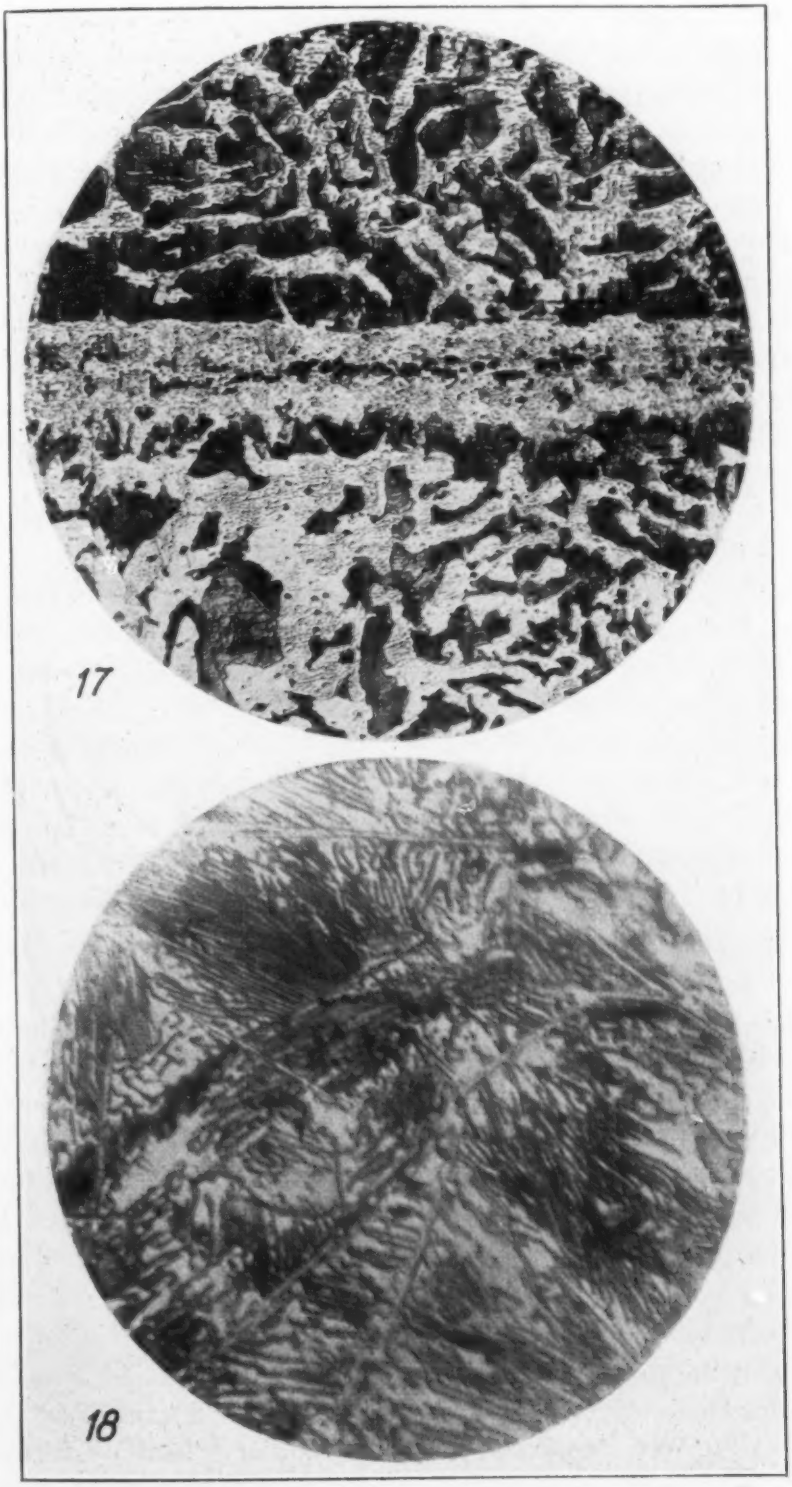

Fig. 17—Sulphide Seam in 0.40 per cent Carbon Steel Etched with Picric Acid. × 100.

Fig. 18—Carburized Structure of Electrolytic Iron. Vacuum-melted and Vacuum-distilled. × 500.

it is difficult to get this much oxygen to go into solution in liquid steel, and Tritton and Hanson (18) have indicated that the solid solubility of oxygen in pure iron is about 0.05 per cent in the absence of any carbon. It is possible that in Grossmann's experiments some of the absorbed oxygen might have been present in some form other than that of solid solution.

A point of interest here is the carburized structure of a vacuum-melted and vacuum-distilled iron (19) shown in Fig. 18. This structure is quite different from either a typical normal or abnormal steel. The oxygen content of this steel was 0.006 per cent, determination by hydrogen reduction. Vacuum-melted iron-manganese alloys showed a gradual change from this type of structure to a normal structure, the most pronounced change being at about 0.20 per cent of manganese. Iron saturated with iron oxide in the liquid steel showed a completely abnormal structure after carburization. Why did the vacuum-distilled iron not show a pronounced abnormal structure? It appears that Grossmann's explanation does not cover this type of metal or that there are variations in diffusion rates and crystallization characteristics not yet determined. In any event, Grossmann's data, with that presented above, show that oxygen in solid solution is the cause of abnormality whether the oxygen is present in the steel before carburization or is dissolved during carburization, and his data on decarburization and structural changes form a basis for the explanation of many problems of the steel treater.

Ghost Lines

The appearance of ghost lines in steel has been attributed by numerous writers primarily to the crystallization of the ingot. It is unquestionably true that in large ingots "corner ghosts" are very difficult to eliminate. Ghost lines due to segregation of metalloids may be eliminated only by extremes in deoxidation and methods of casting ingots as yet impractical to the steel manufacturer. Ghost lines due to the segregation of nonmetallic matter are, as shown in an earlier section, due to the segregation of sulphides and not silicates. As has been discussed earlier in this paper, it is impossible to prevent micro segregation of sulphides, although it is possible to prevent macro segregation. It is further evident that sulphide segregation plays a very important rôle in promoting ghost-line formation.

To demonstrate that deoxidation has a pronounced effect on

ghost lines, I will refer to a series of heats under investigation at the present time where various amounts of deoxidizer were added, both in the furnace and in the ladle. When 0.07 per cent of silicon, in the form of silico-spiegel, was added to the furnace, it was necessary to add sufficient ferrosilicon to have the steel finish at least 0.15-silicon to prevent the formation of ghost lines. When the amount of silicon as silico-spiegel was increased to 0.10 per cent in the furnace, ghost lines did not appear until the silicon in the ladle was lowered enough to give 0.09 per cent of silicon in the finished product. In both types of deoxidation no evidence of ghost lines and little sulphur segregation were found if the final silicon was kept above the limits given. When the silicon content of the steel dropped to these limits, sulphide segregation increased and ghost lines appeared. It is possible that oxygen as FeO, or MnO in solid solution, would cause ghost lines by changing the characteristics of crystallization of the iron-carbon alloy at a particularly segregated point in the ingot, but the evidence points definitely toward the deoxidation's preventing segregation of sulphur. In any event, ghost-line formation due to sulphide segregation may be overcome by proper methods of deoxidizing the steel. The extent of ghost lines due to sulphur segregation resulting from incomplete deoxidation has been shown in Fig. 10.

The same reasoning should apply to ghost lines which contain high concentrations of phosphorus, inasmuch as proper deoxidation will prevent the segregation of this metalloid just as it will of sulphur.

There appear to be many conflicting unpublished data on the effect of ghost lines on the physical properties of steels. During the two weeks prior to the writing of this paper, I have been told of transverse tests on steel containing ghost lines by the metallurgists of two consumers of steel, in whose experimental work the greatest confidence may be placed. One had observed that metal which contained ghost lines was apt to vary considerably in tensile and impact testing following a certain heat treatment. The other exhibited data which showed that there was absolutely no difference in the metal containing ghost lines and that containing no ghosts under the identical heat treatments described by the other investigator.

In an investigation which is in its infancy and from which therefore strict conclusions cannot be drawn, we have found that material containing ghosts gives much the same physical properties as that in which no ghosts are observed for a given heat treatment and ordinary

analysis. With such contradictory evidence on hand, it is obvious that no general conclusions may be drawn.

Physical Properties

There are practically no data available on the effect of submicroscopic or solid solution oxides on the physical properties of steel. The exceptions to this statement are the results of a considerable amount of work which has been done on the physical properties of iron saturated with FeO (3). The effect of solid solution FeO on the electrical resistivity has been referred to earlier, and the same investigation showed that the ductility, impact strength, and elastic limit decreased very sharply upon the addition of iron oxide to pure iron. The ultimate strength was not changed. The comparison here was made on tests of pure iron reported by Neville and Cain (20) and Thompson (21). There are absolutely no data available on the effect of manganese oxide or silica in solid solution, and from general experience there is only one property which very fine alumina particles appear to affect—that is, the ductility of cast steel (22). Impact tests on commercial quality steel, and silicon and aluminum killed electric furnace laboratory steel, have been given earlier and indicated that the finely divided alumina had no effect on the impact value.

It would appear from the preceding remarks that oxygen present in solid solution is of considerable importance in determining certain physical properties of steel; that finely divided inclusions have, with one exception, practically no effect; and, finally, that we know very little about this subject. Before any worthwhile conclusions may be drawn regarding solid solution material such as oxides and sulphides, it will be absolutely necessary to determine physical properties on steels containing no such material. Until this is done, the effect of small amounts of solid solution material will necessarily be masked by the many other variables which are introduced in steel making.

Alloy Contamination

As to alloy contamination, there is one set of variables not often thought of, and that is the contamination of our plain carbon steels by residual alloys. In a survey of the alloy contamination of plain carbon open-hearth steel, carried on by the Bureau of Mines in cooperation with the Open-Hearth Committee of the American Institute

of Mining and Metallurgical Engineers, it has been found that there is an average combined total of Cu, Cr, Ni, Sn, and Va in plain carbon steel amounting to 0.15 per cent. Surely as large an amount of material as this must have its effect on some of the changes which take place in steel upon heat treatment or hot or cold working. This is particularly true of tin, which hardens steel tremendously during hot working.

Conclusion

Four general conclusions may be drawn with regard to the present status and ultimate solution of the inclusion problem.

1. Before the inclusion problem can be properly evaluated it is necessary that a series of alloys, free from sulphur and oxygen, be prepared, and that the physical properties of these alloys be accurately determined. This would serve as a base line for comparison of commercial steels and present steel-making methods.

2. From available data on various physical properties, it appears that large inclusions are much more harmful than small ones. Most metallurgical departments properly inspect steel for cleanliness at 100 diameters magnification.

3. Oxides and sulphides in solid solution are important when certain metallographic structures are to be avoided, or in some instances obtained. The difficulty of determining the amount of such solid solution material present in a steel has been, and will continue to be, an obstacle to the progress of this phase of steel treating and steel making.

4. The steel maker supplies the consumer with steel to a given chemical analysis, combined, in many instances, with a physical, grain size, or cleanliness specification. Oftentimes the filling of one specification will make it very difficult to meet another, and it is on this point that the consumer should most certainly put considerable thought. A higher manganese specification will promote greater cleanliness and a higher silicon specification will give freedom from at least one type of ghost line. The consumer is often entirely to blame for the kind of steel he gets because his specifications do not allow the steel maker to use available materials to the best advantage, and in some instances force him to use these materials to his own and the consumer's disadvantage. At some not too distant day the art of steel making will be superseded by the science of steel making, but the consumer must play his proper rôle in this change.

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CORRELATION OF THE CRYSTAL STRUCTURES AND HARDNESSES OF NITRIDED CASES

By Oscar E. Harder and George B. Todd

Abstract

Samples of open-hearth ingot iron, S.A.E. 1025 steel, a chromium-aluminum nitriding steel, and two chromium-aluminum-molybdenum nitriding steels have been nitrided 72 hours at 975 degrees Fahr. The specimens have been subjected to X-ray examination, hardness tests, and microscopic examination in the original surface and at various depths below the surface.

The ingot iron showed the hexagonal lattice only in the original nitrided surface, while all the other samples showed both the hexagonal and the face-centered cubic lattices in the original surfaces.

At a depth of 0.003 to 0.004 inch below the surfaces all of the samples except the S.A.E. 1025 showed the lattice of alpha iron only, the sample of S.A.E. 1025 showing a weak pattern of the face-centered cubic lattice. At depths of 0.003 to 0.004 inch below the surface the hardness of the nitriding steels was essentially as high as at the surface. In two of the samples it was somewhat higher. The conclusion is drawn that in the case of the nitriding steels the depth of the hexagonal lattice was extremely small and that the face-centered cubic lattice is removed by a cut of 0.003 to 0.004 inch, and that these phases are not necessary in nitrided steels to give a high degree of hardness. The suggestion is made that cases of sufficiently high hardness might be obtained without the production of any of the hexagonal lattice by modifications of the nitriding procedure or by the use of special steels.

Introduction

THERE has been a considerable amount of work done on the crystal structures found in nitrided steels, although there is still

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a lack of complete agreement. Because of the importance of the hardness of nitrided cases, hardness testing has become a well established method of examination, both in research and in production inspection. As a result, much information is available with reference to the hardnesses produced in different nitriding treatments and the depth-hardness curves for different steels and treatments. However, there has been very little work published to show the correlation between the hardness and crystal structure of the different steels at different depths in the case, etc. This investigation had for its objective the correlation of these properties. Some consideration was also given to the microstructures.

Crystal Structures in the Iron-Nitrogen System

From stoichiometric relation Noyes and Smith (10)[1] considered the possible compounds in the iron-nitrogen to be Fe_8N, Fe_6N, Fe_4N, and Fe_2N. Epstein (4), using the work of Noyes and Smith as a guide in assigning the formulas to the different phases, suggested the compounds Fe_6N, Fe_4N, and Fe_2N, and drew a tentative diagram based on thermal analyses, microstructures, and some X-ray work. Previously, diagrams had been prepared by Sawyer (13) and by Fry (5). Epstein noted body-centered cubic, face-centered cubic, and hexagonal close-packed lattices in nitrided cases of electrolytic iron. Hägg (6) has reported four phases in the iron-nitrogen system. These phases are listed below with certain important characteristics.

Phase	Formula	Nitrogen Content Per Cent	Lattice (1)	Parameter in Å a	b	c	Remarks
Alpha	Solution of Nitrogen in Alpha-Iron	0.015—	B. c. c.				
Gamma'	Fe_4N	5.9	F. c. c.	3.789			
Epsilon	Fe_8N	7.7	H. c. p.	2.695—2.767		4.362—4.417	Solid solution with nitrogen 7.7—11%
Zeta	Fe_2N	11.14	Orth.	2.767	4.793	4.417	Indefinite

(1) B. c. c. = body-centered cubic; F. c. c. = face-centered cubic; H. c. p. = hexagonal close-packed; and Orth. = orthorhombic. Å = Angstrom unit = 10^{-8} cm.

Hägg worked with iron powders, which he generally nitrided at 500 degrees Cent. (930 degrees Fahr.). His samples were cooled rather rapidly by moving the container to a cold end of the porce-

[1]The references used in the text will be found in the bibliography appended to this paper.

lain tube, which constituted the nitriding chamber. Some of his samples were also prepared by first nitriding to a high nitrogen content, and then heating in a vacuum, thus removing part of the nitrogen. The nitrogen content of the various samples was determined by heating to 1000 degrees Cent. (1830 degrees Fahr.) for five minutes in a vacuum, noting the loss due to removal of the nitrogen.

Osawa and Iwaizumi (11) noted the hexagonal close-packed lattice but attributed it to the compound Fe_2N with lattice constants "a" = 2.743Å and the c/a ratio as 1.59. They also noted a face-centered cubic lattice with a parameter of 3.86Å and assigned it to the compound Fe_4N. These investigators and Hägg consider that this compound has a nitrogen atom at the center of each elementary cube.

Mehl and Barrett (9) recovered "nitride plates" from specimens of "decarburized mild steel," which had been nitrided 90 hours at 540 degrees Cent. (1005 degrees Fahr.), by dissolving out the surrounding material with concentrated picric acid to which a little nitric acid had been added. These plates were subjected to X-ray analysis and found to give lines in agreement with those assigned to Fe_3N by Hägg and to Fe_2N by Osawa and Iwaizumi (11).

Since Mehl and Barrett (9) noted the plates or needles as the first phase which appeared in alpha iron, they concluded that this phase was the compound of lowest nitrogen content and that it separated from the solid solution on cooling. They do not seem to have considered the possibility of the original formation during nitriding of the plates along crystallographic planes of the alpha iron. This possibility is rather strengthened by their observation that the plates could not be put into solution by reheating 70 hours at the nitriding temperature and then quenching from that temperature. Neither do they seem to have considered the relative solubilities of the different iron-nitrogen phases in the picric-nitric acid reagent. Epstein and others have shown that the phases richer in nitrogen are resistant to picric-nitric acids. If Mehl and Barrett dissolved the Fe_4N phase in the reagent used but did not dissolve the Fe_3N phase, then their results would be in general agreement with those of other investigators.

If Mehl and Barrett recovered their "plates" from the original nitrided surface and then made their microscopic examinations at a depth of 0.002 to 0.003 inch below the surface, they may easily have

gotten the results reported. For example, Fig. 10 in this paper presents a similar structure, which was found at a depth of 0.003 inch below the surface of nitrided Armco iron, which on the original surface showed only the hexagonal lattice. At this depth, however, only the alpha iron lattice was found.

Rieber (12) has reported the compound Fe_5N_2, in which the nitrogen content is 9.73 per cent. However, if the compound Fe_3N has the range of solubility for nitrogen reported by Hägg, it would be possible to have an alloy containing 9.73 per cent and still have a solid solution. (Hägg's epsilon phase.)

The dissociation pressure of iron nitrides has been the subject of a number of researches. Noyes and Smith, previously mentioned, reported values 20,000 to 500,000 atmospheres. Emmet, Hendricks, and Brunauer (3) have recently determined the dissociation pressure for Fe_4N at 444 degrees Cent. (825 degrees Fahr.) as 5000 atmospheres. A dissociation pressure of 50,000 atmospheres has been reported for Fe_2N. These observations are in agreement with the difficulties found in trying to form nitrides from molecular nitrogen and iron. It thus seems that all the iron nitrides are metastable and should decompose, even at ordinary temperatures.

Hägg found that the nitrides richest in nitrogen began to dissociate at about 500 degrees Cent. (930 degrees Fahr.) and that at 600 degrees Cent. (1110 degrees Fahr.) the pressure was greater than 200 atmospheres. Maxted (8), using nitrided finely divided iron, also found the dissociation pressure at 600 degrees Cent. (1110 degrees Fahr.) to be greater than 200 atmospheres.

Charpy and Bonnerot (1) found that Fe_4N was not dissociated before reaching 600 degrees Cent. (1110 degrees Fahr.). Above that temperature a nitrogen pressure of 18 atmospheres reduced the rate of dissociation but did not completely prevent it.

The above data indicate that the higher the nitrogen content of the compound the greater the dissociation pressure. These relations have an important bearing on the use of nitrided products at elevated temperatures. Actual tests have shown that nitrided parts and test specimens will retain practically full hardness after heating as long as 200 hours at 450 degrees Cent. (840 degrees Fahr.), and reports are available which show only slight losses in hardness after heating as high as 650 to 700 degrees Cent. (1200 to 1300 degrees Fahr.). This probably means that the higher nitrides were not present in the cases.

Purpose of Present Investigation

The present investigation had for its purpose a correlation of the crystal structures as determined by the X-ray diffraction method, the hardness as determined by the Vickers indenter, and the microstructures of the original surfaces produced on nitrided materials and of those cases at different depths from the surface.

Naturally, the tests as outlined above throw some light on the phases present in the nitrided cases of the different kinds of steel investigated and the changes in the phases present at different depths in the case.

Materials. Materials used in this investigation included an open-hearth iron, a medium carbon steel, and three commercial nitriding steels, No. 3 of which was one of the early nitriding steels, while Nos. 4 and 5 are later developments.

The open-hearth ingot iron and S.A.E. 1025 steel were used in the "as-rolled" condition. The nitriding steels Nos. 4 and 5 were used in the "as received" condition, which in this case represented material which had been quenched and tempered by the manufacturer. Sample No. 3 was heated to 857 degrees Cent. (1575 degrees Fahr.), quenched in water, and then tempered at 600 degrees Cent. (1110 degrees Fahr.) for 1½ hours. The compositions of these various steels are given in Table I.

Table I
Materials Used in Investigation

Sample Number	Chemical Composition							
	C	Mn	Si	P	S	Al	Cr	Mo
1*	0.013	0.017	....	0.005	0.025	....	....	....
2	0.27	0.50	....	0.014	0.038	....	....	....
3*	0.44	0.50	0.34	0.014	0.020	0.84	1.61	....
4*	0.36	0.51	0.27	0.013	0.010	1.23	1.49	0.18
5*	0.23	0.51	0.20	0.011	0.011	1.24	1.58	0.20

*Manufacturer's typical analysis.

The specimens used in this investigation were $\frac{11}{16}$ x ⅛ x ⅛-inch. Specimens were first shaped on a surface grinder and then polished on 000 emery paper on two adjacent sides before nitriding. This specimen was used for X-ray and microscopic examination, as well as for the hardness tests.

Apparatus. The nitriding equipment was the same as that previously described by Harder, Gow, and Willey (7). The X-ray diffraction apparatus was the type VWC, form B, devised by Hull,

and made by the General Electric Co. Special equipment had to be introduced, in order to make use of the surfaces of these small nitrided specimens.

The blocks were held in a wooden jig, which is shown as "B" in Figs. 1 and 2. This arrangement made it possible to use the polished surface of the nitrided specimen for X-ray examination.

The hardness tests were made by the Vickers method, using a load of 10 kilograms, which was applied for thirty seconds.

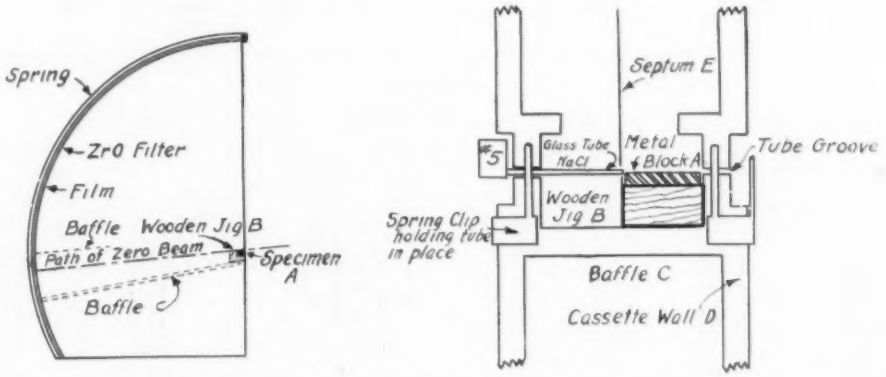
Nitriding Treatment. The specimens were all nitrided at the same time at a temperature of 523 degrees Cent. (975 degrees Fahr.). The nitriding time was 72 hours, and the average decomposition of the ammonia was approximately 20 per cent. The specimens were slowly cooled in the furnace in a stream of ammonia to about 90 degrees Cent. They were then polished with emery and rouge, care being taken so that not more than 0.0002 to 0.0003 inch was removed in polishing. They were then in turn subjected to X-ray examination, microscopic examination, and finally to hardness testing.

X-Ray Examination

The specimens were etched in a special etching reagent of ten parts of 4 per cent picric acid in ethyl alcohol and one part of 4 per cent nitric acid, also in ethyl alcohol. The etched blocks were then adjusted in the cassette shown in Figs. 1 and 2. The grazing angle of the X-ray beam was approximately 5 degrees. For comparison purposes, one side of the cassette was filled with a 50-50 mixture of sodium chloride and starch. The X-ray exposures were made at 15-20 milliamperes filament current, and the time varied from 48-66 hours.

The X-ray films were read in a holder in the manner described by Davey (2). The films showing the alpha iron lattices were placed with the (2 1 1) plane at 1.167Å, which is the calculated value for a unit parameter of 2.86Å. The films showing the Fe_4N (face-centered cubic) lattice were adjusted with the line for the 2 0 0 plane at 1.900, which is the calculated value for the lattice using a parameter of 3.80 Å, which is in good agreement with Hägg's value for this line. Fortunately, these two patterns appeared in all films except two, those of the original nitrided surfaces of the Armco and the S.A.E. 1025 blocks. Because of the good agreement between the spacings of the film for the 1025 steel and Hägg's Fe_3N values, setting the fourth

line (10.2) on 1.624 Å, seemed justified. In the Armco film the (10.2) line was very weak, and the (11.0) line was set on 1.376 Å, which was the value found for this line in the 1025 steel. The cal-



Figs. 1 and 2—Arrangement of Specimens for X-Ray Examination.

culations of the unit parameters for the face-centered and body-centered lattices were by the usual methods.

Calculations for the hexagonal lattices are based on the two equivalent equations:

$$(1)\quad \sin^2\Theta = \frac{\lambda^2}{3a^2}\left(h^2 + hk + k^2 + \frac{3a^2\,l^2}{4c^2}\right)$$

$$\text{and}\quad (2)\quad \sin^2\Theta = \frac{\lambda^2}{3a^2}\left(h^2 + hk + k^2\right) + \frac{\lambda^2\,l^2}{4c^2}$$

in which Θ is the angle of reflection; λ the X-ray wave length; h, k, and l are indices of the planes of reflection; a is the unit side of the hexagon, and c the altitude.

By beginning with close approximation for the c/a ratio, it is possible to calculate the average value of a and then the c value. In this work the c/a ratio was known to be about 1.6. From the average values for a and c the true c/a ratio was finally calculated.

Theoretical Values of Lattices. The theoretical values for the interplanar distances for the various planes were calculated using the unit parameters 2.860 and 3.80 Å for alpha iron and Fe_4N, and the results are shown in Table II. The values for the hexagonal close-packed phase (Fe_3N) in the same table are Mehl and Barrett's conversion of Hägg's data.

Examination of Nitrided Samples. All samples were examined at the orginal surface and at four depths below the surface; the last

section examined was near the core. Table III shows the amount of case removed in the various cuts and the hardness of the cases at these different depths. The hardness values are represented graphically in Fig. 3. It will be observed that some 0.003 to 0.004 inch of

Table II

Theoretical Interplanar Spacings of Alpha Iron, Fe_4N and Fe_3N

Alpha iron phase B. C. C. a=2.860 A		Fe_4N phase F. C. C. a=3.80 A		Fe_3N phase * H. C. P. a=2.767; c=4.417 A	
Indices	Spacings	Indices	Spacings	Indices	Spacings
110	2.022	111	2.194	10.0	2.399
200	1.430	200	1.900	00.2	2.210
211	1.167	220	1.344	10.1	2.107
220	1.011	311	1.146	10.2	1.624
310	0.904	222	1.097	11.0	1.403
222	0.826	400	0.950	10.3	1.256
321	0.764	331	0.872	20.0	1.199
400	0.715	420	0.850	11.2	1.173
411	0.674	422	0.776	20.1	1.157
420	0.640	511	0.731	00.4	1.104
332	0.610	440	0.672	20.2	1.054
422	0.584	531	0.642	10.4	1.003
431	0.561	600	0.633	20.3	0.929
521	0.522	...	....	12.1	0.888
				11.4	0.863

*Values found by Hägg for a sample containing 11.1 per cent nitrogen, which he concluded represented about the maximum solubility of nitrogen in Fe_3N. Ratio c/a = 1.596.

case was removed in each cut. Samples 3 and 4 showed a slight increase in hardness after the removal of the first cut.

The Original Nitrided Surface. The data from the X-ray examination of the original nitrided surfaces are given in Table IV, and the patterns are shown in Fig. 4. The values for interplanar spacings and unit parameters in Table IV are all in Angstrom units.

The Armco iron, sample No. 1, showed only the hexagonal close-packed pattern. All other samples showed both the hexagonal and the face-centered cubic lattices. The unit parameters of the Armco iron lattice show expansion; in fact both a and c are greater than the maximum values reported by Hägg (See Table II). This expansion may be interpreted to mean a high nitrogen content. The c/a ratio, however, is higher than Hägg reported and does not agree with Hägg's findings that as the a and c parameters increase the c/a ratio decreases.

The S.A.E. 1025 steel, sample No. 2, gave both the hexagonal and the face-centered cubic patterns, but the latter was somewhat indefinite. Both the a and c parameters are expanded.

Samples Nos. 3, 4, and 5 showed both patterns, and the lines

Table III

Relation of Depth of Cut and Vickers-Brinell Hardness Numbers

Sample Number	Depth of Cut in Inches			
	1st Cut	2nd Cut	3rd Cut	4th Cut
1	0.0031	0.0077	0.0108	0.0177
2	0.0026	0.0064	0.0111	0.0169
3	0.0036	0.0085	0.0124	0.0176
4	0.0036	0.0080	0.0123	0.0183
5	0.0041	0.0083	0.0123	0.0185

Sample Number	Vickers-Brinell Hardness					
	Unnitrided	Surface	1st Cut	2nd Cut	3rd Cut	4th Cut
1	128	155	131	127	131	130
2	130	211	200	173	172	176
3	280	999	1026	853	661	401
4	194	955	967	795	528	356
5	181	911	901	833	673	371

These data are shown graphically in Fig. 3.

were about equally strong. It should be noted that the line for the 2 0 0 plane in the face-centered cubic lattice is the distinctive line and appears in all of these alloy steel patterns. These results seem to indicate that the surface layers of these alloy nitriding steels contain

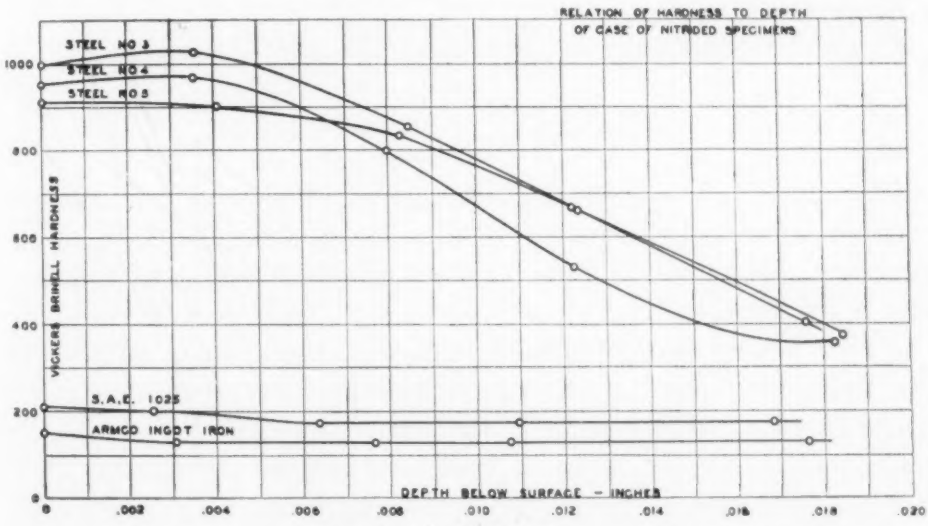


Fig. 3—Relation of Hardness to Depth of Case of Nitrided Specimens.

two phases which are probably those designated by Hägg as gamma′ and epsilon.

Since the hexagonal lattice found in nitrided cases exhibits variable parameters, it is of interest to compare the values found by the different investigators. In Table V which follows the values for samples Nos. 1-5 are those found in the present research, and the other values are those found by others, as indicated.

Microstructures of Specimens Tested

The microstructures of the original nitrided surfaces are shown in Figs. 5 to 8 inclusive. All photomicrographs were taken at a magnification of 1000. The etchant used throughout was picric acid to which a little nitric acid had been added. The time required for

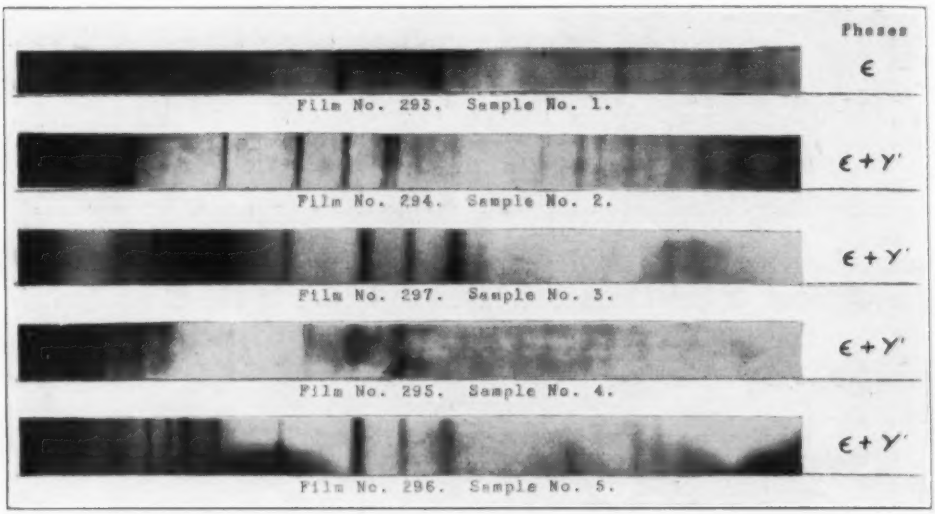


Fig. 4—X-ray Spectrograms of Original Nitrided Surfaces.

etching varied with the depth of cut and somewhat with the different materials. The original surface of the alloy steels required 45 seconds to one minute, while for some of the later cuts the etching time was only a few seconds.

Fig. 5 shows the original structure of the Armco iron, and it will be observed that it appears to be a single phase, with the possible exception of slight porosity. In correlation with the X-ray data this appears to be a solid solution, which exhibits the hexagonal close-packed lattice. A complete interpretation of the apparent porosity is not possible. The partial decomposition of some of the nitrides originally formed in the surface of the case has some evidence for its support. Reduction of oxides by hydrogen must also be considered.

The original structure for the S.A.E. 1025 steels is shown in Fig. 6. On first examination this structure appears to be homogeneous, except for some porosity. However, on close examination it will be observed that there are certain areas which show lighter colors than others, so that this microstructure might correspond with

Table IV

X-Ray Data of Original Nitrided Surfaces

Line Number	Index H. c. p.	Index F. c. c.	Interplanar Spacing	Intensity*
		Sample No. 1 (Film No. 293)		
1	10.0		2.39	s.
2	10.1		2.10	s.
3	10.2		1.624	v.w.
4	11.0		1.375	s.
5	10.3		1.259	v.w.
6	11.2		1.170	w.
7	20.1		1.149	m.
8	20.2		1.050	v.w.
9	20.3		0.928	v.w.
10	12.1		0.879	v.w.
11	11.4		0.859	v.w.
12	10.5		0.830	v.w.
13	20.4		0.807	v.w.
14	12.3		0.767	v.w.
	H. c. p.	a=2.746 c=4.449 c/a=1.620		
		Sample No. 2 (Film No. 294)		
1	10.0		2.40	m.
2	00.2	111	2.235	m.
3	10.1		2.11	v.s.
4	10.2		1.624	m.
5	11.0	220	1.376	s.
6	10.3		1.256	m.
7	11.2		1.170	m.
8	20.1	311	1.149	m.
9	00.4	222	1.108	v.w.
10	20.2		1.051	v.w.
11	10.4		1.008	v.w.
12	20.3		0.929	w.
13	12.1	331	0.878	w.
14	11.4	420	0.859	v.w.
15	10.5		0.830	v.w.
16	20.4		0.810	v.w.
17		422	0.791	v.w.
18	12.3		0.766	v.w.
19	10.6		0.709	v.w.
20	11.6		0.654	v.w.
21	12.5		0.630	v.w.
	H. c. p. a=2.745 c=4.445 c/a=1.619	F. c. c. a=3.850		
		Sample No. 3 (Film No. 297)		
1	10.0		2.33	s.
2	00.2	111	2.18	s.
3	10.1		2.055	s.
4		200	1.901	s.
5	10.2		1.597	m.
6	11.0	220	1.349	s.
7	10.3		1.237	s.
8	11.2	311	1.146	s.
9	00.4	222	1.098	v.w.
10	12.1	331	0.872	v.w.
11	11.4	420	0.848	v.w.
12	10.5		0.825	v.w.
	H. c. p. a=2.697 c=4.352 c/a=1.614	F. c. c. a=3.799		

Table IV—Continued

Line Number	Index H. c. p.	Index F. c. c.	Interplanar Spacing	Intensity*
		Sample No. 4 (Film No. 295)		
1	10.0		2.35	m.
2	00.2	111	2.19	m.
3	10.1		2.075	s.
4		200	1.900	m.
5	10.2		1.605	w.
6			1.42 (?)	
7	11.0	220	1.358	m.
8	10.3		1.244	m.
9	11.2	311	1.149	m.
10		400	0.951	w.
11	20.3		0.917	w.
12	12.1	331	0.874	w.
13	11.4	420	0.852	w.
	H. c. p. a=2.713 c=4.320 c/a=1.592		F. c. c. a=3.807	
		Sample No. 5 (Film No. 296)		
1	10.0		2.35	m.
2	00.2	111	2.188	m.
3	10.1		2.07	s.
4		200	1.901	m.
5	10.2		1.596	m.
6	11.0	220	1.351	s.
7	10.3		1.238	m.
8	11.2	311	1.144	m.
9		400	0.950	v.w.
10	12.1	331	0.869	v.w.
11	11.4	420	0.848	v.w.
	H. c. p. a=2.703 c=4.376 c/a=1.619		F. c. c. a=3.796	

*The intensities of the lines in the diffraction patterns have been indicated by the following:

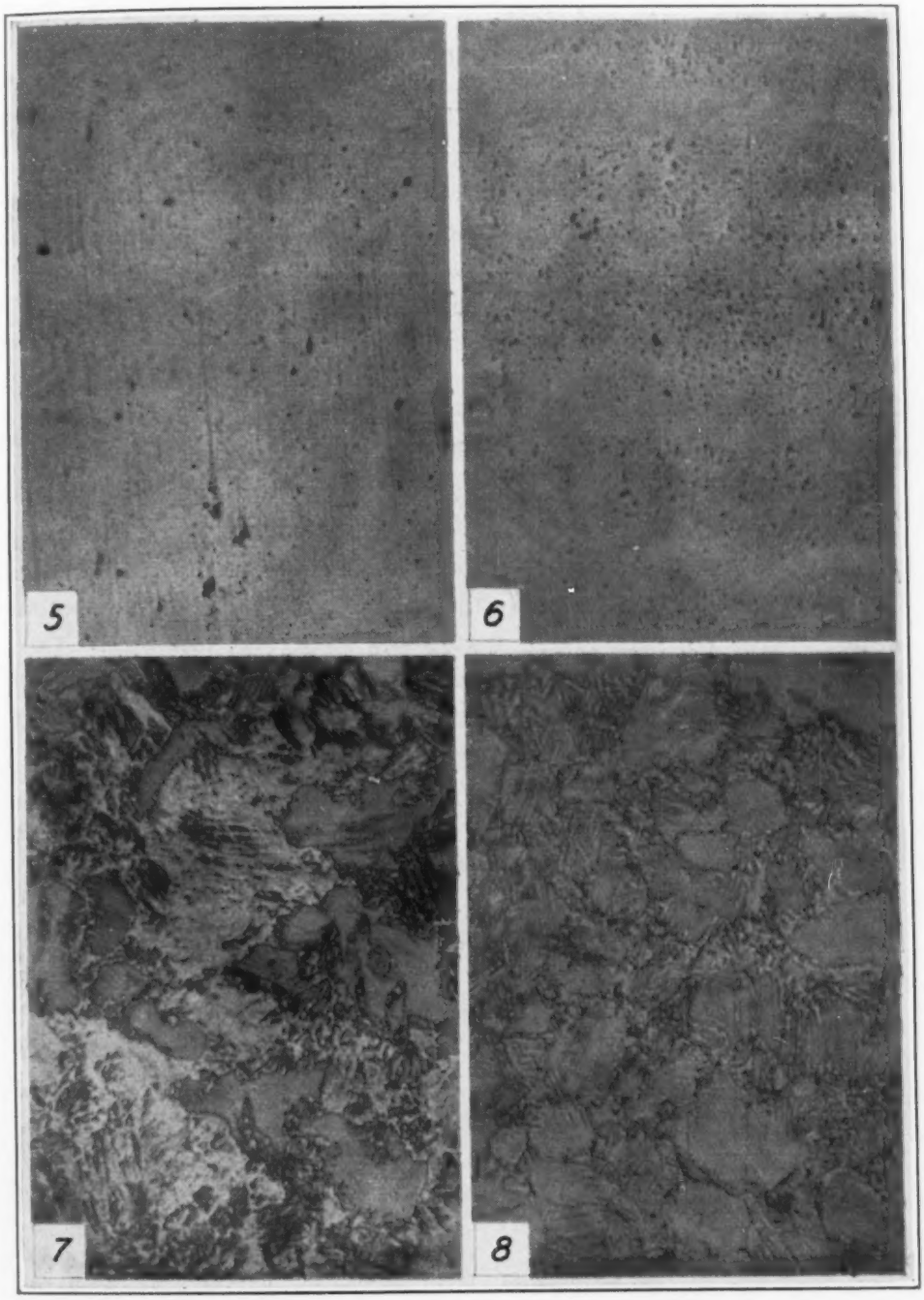
v.s.=very strong
s.=strong
m.=medium
w.=weak
v.w.=very weak

Table V

Unit Parameters of the Iron-Nitrogen Hexagonal Phase

(All values are in Angstrom Units)

Sample Number	Unit Parameters a	Unit Parameters c	Ratio c/a
1	2.746	4.449	1.620
2	2.745	4.445	1.619
3	2.697	4.352	1.614
4	2.713	4.320	1.592
5	2.703	4.370	1.619
Hägg— 8.6% Nitrogen	2.70	4.370	1.617
Hägg—11.1% Nitrogen	2.767	4.417	1.596
Osawa and Iwaizumi— 8.08% Nitrogen	2.733	4.402	1.611
Osawa and Iwaizumi— 9.09% Nitrogen	2.756	4.402	1.598
Osawa and Iwaizumi—11.0 % Nitrogen	2.745	4.407	1.594



PHOTOMICROGRAPHS OF NITRIDED SPECIMENS

Fig. 5—Original Surface of Nitrided Open-hearth Iron. × 1000.
Fig. 6—Original Surface of Nitrided S.A.E. Steel 1025. × 1000.
Fig. 7—Original Nitrided Surface of Sample No. 4. × 1000.
Fig. 8—Original Nitrided Surface of Sample No. 5. × 1000.

the X-ray film which showed a strong hexagonal pattern and a weak face-centered cubic pattern.

The microstructure of sample No. 3 was quite complicated and difficult of interpretation, and on that account has not been included.

Fig. 7 shows the microstructure of sample No. 4. This is a 0.36 per cent carbon nitriding steel. The X-ray pattern had shown a duplex structure, and such a structure is also indicated in the photomicrograph. Our interpretation would be that the unattacked areas represent the epsilon phase, while the lighter areas showing attack represent the face-centered cubic or Fe_4N phase.

Fig. 8 shows the microstructure of sample No. 5, which is a lower carbon nitriding steel. Apparently the amount of the epsilon phase is greater in this steel than in the higher carbon steel (No. 4), which was otherwise of the same analysis.

The hardness of the original surfaces of these steels are given in Table III and in Fig. 3. Some tendency toward brittleness was observed in the tests on the original nitrided surfaces, thus associating brittleness with the hexagonal crystal structure. In the first cut on sample No. 2 the face-centered cubic lattice was found, but no indication of brittleness was observed. This gives some evidence that brittleness is not due to the Fe_4N phase.

The First Cut Below the Surface. The amount of material removed in the first cut on the different samples is shown in Table III. It will be observed that the amount of material ranged from about three to four thousandths.

The data from the X-ray examination of samples after the first cuts were taken off are shown in Table VI, and the films representing the X-ray photograms for the different samples are shown in Fig. 9.

It is interesting to note that in the case of the Armco iron the removal of 0.0031 inch not only removed the material which produced the hexagonal pattern but also the material which presumably was present which would produce the face-centered cubic lattice, and this film shows only the body-centered cubic lattice. In the case of the S.A.E. 1025 steel the hexagonal pattern is completely removed, but there is present a duplex pattern representing the Fe_4N and the alpha iron phases. The presence of carbon in this steel, as compared with the Armco iron, may have favored the formation and penetration of the face-centered cubic lattice; however, small amounts of alloying

Table VI

X-Ray Data of the First Cut Below the Surface of Nitrided Specimens

Line Number	Index B. c. c.	Index F. c. c.	Interplanar Spacing	Intensity
		Sample No. 1 (Film No. 299)		
1	110		2.010	v.s.
2	200		1.430	s.
3	211		1.167	v.s.
4	220		1.012	w.
5	310		0.903	m.
6	222		0.825	v.w.
7	321		0.762	m.
8	400		0.714	v.w.
9	411		0.684	v.w.
10	332		0.610	v.w.
11	422		0.584	v.w.
12	431		0.561	v.w.
		B. c. c. a=2.859 A. U.		
		Sample No. 2 (Film No. 300)		
1			2.35	v.w.
2		111	2.175	v.s.
3	110		2.01	m.
4		200	1.886	v.w.
5	200		1.429	m.
6		220	1.339	w.
7	211		1.167	v.s.
8		311	1.143	v.w.
9	220		1.010	m.
10	310		0.905	m.
11	321	422	0.764	m.
12	411	440	0.674	v.w.
13	420	531	0.640	v.w.
		B. c. c. a=2.859 A. U. F. c. c. a=3.779 A. U.		
		Sample No. 3 (Film No. 303)		
1	110		2.02	s.
2	200		1.431	w.
3	211		1.168	m.
4	220		1.010	v.w.
5	310		0.905	v.w.
6	321		0.765	v.w.
		B. c. c. a=2.860 A. U.		
		Sample No. 4 (Film No. 301)		
1	110		2.01	s.
2	200		1.427	m.
3	211		1.167	m.
4	220		1.011	w.
5		400	0.949	w.
6	310		0.905	w.
7			0.866	v.w.
8			0.845	v.w.
9	222	?	0.827	v.w.
10			0.814	v.w.
11	321		0.764	v.w.
12	411		0.675	v.w.
		B. c. c. a=2.860 A. U. Doubtful lines may belong to hexagonal pattern.		
		Sample No. 5 (Film No. 302)		
1	110		2.015	s.
2	200		1.424	m.
3	211		1.167	s.
4	220		1.010	v.w.
5	310		0.905	m.
6	222		0.827	m.
7	321		0.764	m.
		B. c. c. a=2.858 A. U.		

elements as are usually found in commercial steels were present, and they may have had an influence on the phases present.

In the case of the nitriding steels—samples Nos. 3, 4, and 5—this first cut removed both the hexagonal and the face-centered cubic lattice, and we have only the lattice characteristic of alpha iron. In the case of sample No. 4 there was one weak line which belongs

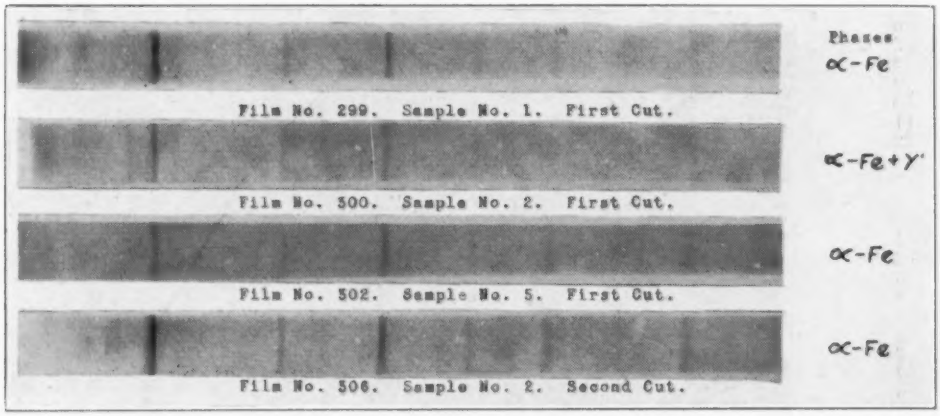
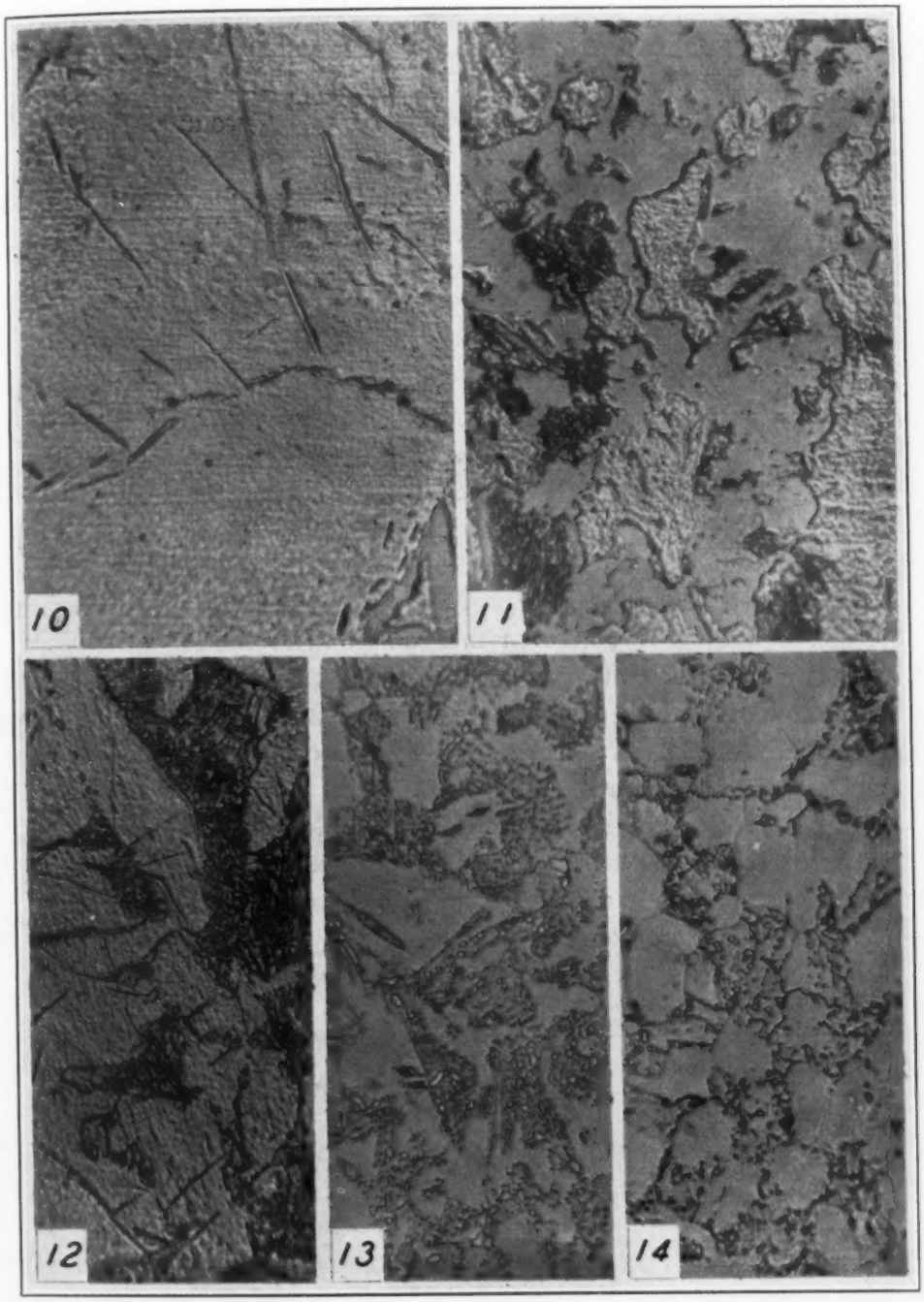

Phases
α-Fe
Film No. 299. Sample No. 1. First Cut.
α-Fe+γ'
Film No. 300. Sample No. 2. First Cut.
α-Fe
Film No. 302. Sample No. 5. First Cut.
α-Fe
Film No. 306. Sample No. 2. Second Cut.

Fig. 9—X-ray Spectrograms of First and Second Cuts of Nitrided Cases.

to the face-centered cubic lattice. In this connection it is of importance to point out that, although the first cut removed all the phases except the alpha iron solid solution, the samples retained full hardness, as shown in Table III; in fact, samples Nos. 3 and 4 showed a slightly greater hardness after the removal of the first cut than they did as tested on the original surface. The failure of these samples to show more than one lattice is not positive proof that a second phase is not present, but it does show that there is no other phase present in sufficient concentration or size of particle to give a diffraction pattern. The findings from the X-ray examination are in agreement with the results of the microscopic examination which are discussed later. This naturally raises the question whether or not the useful, rather tough, case produced in nitriding may be entirely due to the alpha phase—a solution of nitrogen in alpha iron.

In the reproduction of the films in Fig. 9 the films for samples Nos. 3 and 4 are not shown, because they are similar to the film for sample No. 5. Film No. 306 is included in this group in order to show that the face-centered cubic pattern found in the first cut of the S.A.E. 1025 steel had completely disappeared after the second cut



PHOTOMICROGRAPHS OF NITRIDED SPECIMENS. × 1000.

Fig. 10—First Cut of Nitrided Open-hearth Iron.
Fig. 11—First Cut of Nitrided S.A.E. 1025 Steel.
Fig. 12—Second Cut of Nitrided S.A.E. 1025 Steel.
Fig. 13—First Cut of Nitrided Sample No. 4.
Fig. 14—First Cut of Nitrided Sample No. 5.

which had removed 0.0064 inch of the case. The corresponding microstructure is shown in Fig. 12.

The Microstructures of the First Cut. The microstructure of the Armco ingot iron is shown in Fig. 10. The ground mass is apparently the alpha iron solid solution. The frequently observed nitride needles, or as Mehl and Barrett have termed them, "nitride plates," are in evidence, and there is some material collected at the grain boundary. However, on X-ray examination, there is not a sufficient amount of this minor phase present to give an X-ray diffraction pattern.

The structure of the S.A.E. 1025 steel is shown in Fig. 11. The X-ray pattern showed that there were two phases present—the face-centered cubic and the alpha iron phase. Our interpretation of the microstructure is that the background is the alpha iron phase. The lighter appearing microstructure, which shows etching attack, but which seems to be somewhat in relief, is apparently the Fe_4N phase. The darker structure, which appears in relief, is undoubtedly pearlite. Another interesting structure of this sample after the second cut was taken off shows the complete absence of the gamma phase, but shows the alpha phase with nitride needles. This structure is shown in Fig. 12. Consistently the X-ray pattern shows only the body-centered cubic lattice to be present.

Fig. 13 shows the structure of sample No. 4 after the first cut. This is the 0.36 per cent carbon nitriding steel, and the structure is apparently that of the alpha phase, with some spheroidized carbide particles. This structure showed only the body-centered cubic lattice.

Fig. 14 shows the microstructure of sample No. 5 after the first cut has been removed. Here again the structure seems to be that of the alpha phase, in which there is embedded the carbide particles, mostly in the spheroidized condition. This again is consistent with the X-ray diffraction pattern which showed only the body-centered cubic lattice. The microstructure of sample No. 3 was not reproduced, because it was quite similar to those of samples Nos. 4 and 5.

Examination of the Second, Third, and Fourth Cuts Below the Surface. The complete examination was made of all of these specimens at the second, third, and fourth cuts below the surface, the depths of which are shown in Table III. The results of the examination of Sample No. 2—S.A.E. 1025 steel—have already been discussed. Otherwise, no change in the structure was observed.

The X-ray examination showed only the alpha iron lattice, and since this lattice does not appear to have its parameter changed by the addition of nitrogen, no variation in the unit parameter would be expected at the different depths in the nitrided case. There was some variation in the diffuseness of the lines, but no definite correlations could be made. If distortion of the alpha iron lattice results from the solution of nitrogen, then one might attempt to correlate the character of the lines and the nitrogen content. In these experiments, however, light cuts of the nitrided surface were removed by grinding, and it would be impossible to tell whether a distorted lattice was due to nitrogen in solution or strains introduced in grinding. Microscopic examination of the surface at greater depth showed little, if any, variation.

The nitride needles or plates were found in the Armco iron and the S.A.E. 1025 steel, but they were not evident in the alloy nitriding steels. We were not able to identify definitely a precipitated phase—that is, one which precipitated on cooling—in any of the specimens, unless the needles or plates in the material at the grain boundary in Figs. 10 and 12 represent such a phase. Examination at high magnification might reveal such a phase in the alpha iron solid solution.

General Conclusions

The hexagonal close-packed lattice was found in all of the samples, but it was accompanied by the face-centered cubic lattice in all of the samples, except the Armco iron. The results indicate that for the samples studied in depths below the surface transition is from the hexagonal lattice at the surface, or the hexagonal lattice with the face-centered cubic to the face-centered cubic, and then to the face-centered cubic with the alpha lattice, and that at comparatively small depths—0.003 to 0.004 inch—the alpha lattice only is found.

The hexagonal close-packed lattice seems to be associated with the surface brittleness in nitrided cases. Cases showing the face-centered cubic and the alpha iron lattice were not found to be brittle. Nitrided cases showing the alpha iron lattice only have been found to possess full hardness and even show a greater hardness than the original surface. This leads to the conclusion that extreme hardness of nitrided cases can be accounted for by the presence of nitrogen in solution in the alpha iron lattice, and that while no finely dispersed phase has been found at 1000 magnification and no X-ray

evidence of a second phase has been found, there still remains the possibility of the existence of such a phase in a sub-microscopic size and in such a finely dispersed condition that it will not give an X-ray diffraction pattern.

The technique worked out for the examination of nitrided cases seemed to present a more direct and satisfactory method of study than has previously been reported.

This investigation suggests the desirability of developing nitriding steels or nitriding methods which will make possible the production of nitrided cases which are free from the hexagonal epsilon phase. It might be more satisfactory to obtain a case consisting entirely of the alpha iron phase, since this phase gives the necessary hardness and appears to be free from brittleness.

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DISCUSSION

Written Discussion: By John T. Norton, associate professor of physics of metals, Massachusetts Institute of Technology, Cambridge, Mass.

The authors of this paper are to be congratulated on their interesting descriptions of the structures found in nitrided iron and alloy steel. The X-ray diffraction method of examination is well suited for this work and some important conclusions are to be drawn from their study. The authors have found the same structures in pure iron and in alloy steels and they are identified as nitrides of iron. To be sure, they did not find the face-centered phase in the Armco iron sample, but it has been found in this material by the writer and by others. From this we are forced to conclude that it is not these nitrides of iron which are primarily involved in the hardening process of nitriding alloys because the same nitrides occur in pure iron which does not harden appreciably. We must look to the alloying elements aluminum and chromium and their roles are still a matter of dispute.

The present determination of lattice parameters is not sufficiently precise to show any systematic change due to the presence of these elements. The excellent work on the iron-nitrogen system by Eisenhut and Kaupp,* which perhaps the authors have overlooked, is a beautiful example of the high precision which can be obtained and they have established the major portion of the equilibrium diagram by X-ray means alone. Such work should be extended to include the alloying elements.

It is interesting to note that the maximum hardness is obtained when only the body-centered phase is observed. Some work by the writer has shown that face-centered phase begins to appear at about 2 per cent nitrogen, hence the maximum hardness involves only a small nitrogen content.

It does not seem probable that the diffraction methods will reveal the cause of hardening by the indication of new structure types but rather by small changes of lattice constants or by lattice distortion as shown by broadening of the diffraction lines. For this reason we may only hope to attack the problem by the most precise work of which the method is capable. Such information correlated with the microstructures and physical properties should be of greatest help in finding a solution of these complex alloys.

Written Discussion: By J. T. Norton, Jr., chief chemist, Ludlum Steel Co., Watervliet, N. Y.

The statement made by the authors of this interesting paper that nitrided cases showing the alpha iron lattice only have been found to possess full hardness without objectionable brittleness is of great importance to users of the nitriding process.

It is to be hoped that some method of control will be found so that only this alpha iron lattice will be produced. As a matter of fact, most nitrided parts are given a light grind after hardening which doubtless removes the greater part of the objectionable hexagonal close-packed lattice and thus corrects the brittleness caused by this crystal structure.

I should like to have Dr. Harder's opinion as to just what role such ele-

*Eisenhut and Kaupp. "Das System Eisen-Stickstoff." *Zeitung für Electrochemie*, Bd. 36, Nr. 6, 1930.

ments as chromium, aluminum, vanadium and molybdenum play in nitriding steels and what is the reason for the remarkable effect on surface hardness which these elements appear to cause.

Table III in the paper shows that in the case of sample No. 1 (Armco iron) and sample No. 2 (S.A.E. 1025) very little increase in hardness is produced by nitriding. The addition of approximately only 1 per cent of aluminum and 1.50 per cent of chromium in sample No. 3 and in samples No. 4 and No. 5 of 0.20 per cent of molybdenum in addition to the aluminum and chromium produce after nitriding an increase in hardness which is truly remarkable. This hardening effect has been generally ascribed to the formation of complex nitrides of these elements with iron but no proof has as far as I know been attempted.

In his original paper on the nitriding process Dr. Fry determined the decomposition point of the nitrides of iron, manganese, chromium, tungsten, titanium, vanadium and aluminum. Of all the elements studied, aluminum showed considerably the highest decomposition point followed in order by chromium and vanadium and it is worthy of note that this order is approximately the same in the hardening effect of these elements when introduced into steels.

There is some evidence that more than one element in combination with iron is desirable in a good nitriding steel, for example, a piece of calorized metal in which metallic aluminum is driven into the surface of the steel is not appreciably hardened when nitrided.

Also, all of the well known types of nitriding steels contain two or more elements, such as chromium, aluminum, molybdenum, molybdenum-aluminum, or chromium-vanadium. The role of carbon in nitriding steels is also of considerable interest as it is well known that in nitriding steels the depth of nitrogen penetration as shown by etching reagents decreases as the carbon percentage is raised.

Written Discussion: By Peter R. Kosting, research associate, Bureau of Standards, Washington, D. C.

This timely paper shows a number of interesting photomicrographs, especially those of nitrided open-hearth iron and S.A.E. 1025 steel. A transverse view would have been very enlightening, for then the actual depth and nature of the outermost layer would have been better revealed. With this in view the following are given, which are the results of work suggested by S. B. Hendricks and P. H. Emmett and done while at the Fixed Nitrogen Research Laboratory, Washington, D. C., early in 1930.

Specimens of open-hearth iron (carbon 0.029 per cent; silicon 0.005 per cent; manganese 0.01 per cent) electrolytic iron (carbon 0.019 per cent; silicon 0.01 per cent; manganese trace), as well as iron powder and iron nails were annealed in 3-1 H_2-N_2 gas mixture at 640 degrees Cent. and then nitrided in ammonia gas at 565 degrees Cent. $\pm$ 5 degrees for 96 hours. Such conditions favor the formation of epsilon solid solution. The iron powder analysed 10.1 per cent N_2. Fig. 1 of this discussion shows a transverse view of the edge of an iron nail. The nitride case is around 0.0026-inch thick. An X-ray photogram of the outside of this nail showed both the epsilon and gamma prime patterns. It is estimated that these rays penetrated about 0.001 inches. Fig. 2 shows the differentiation of the outside layer into two parts by pro-

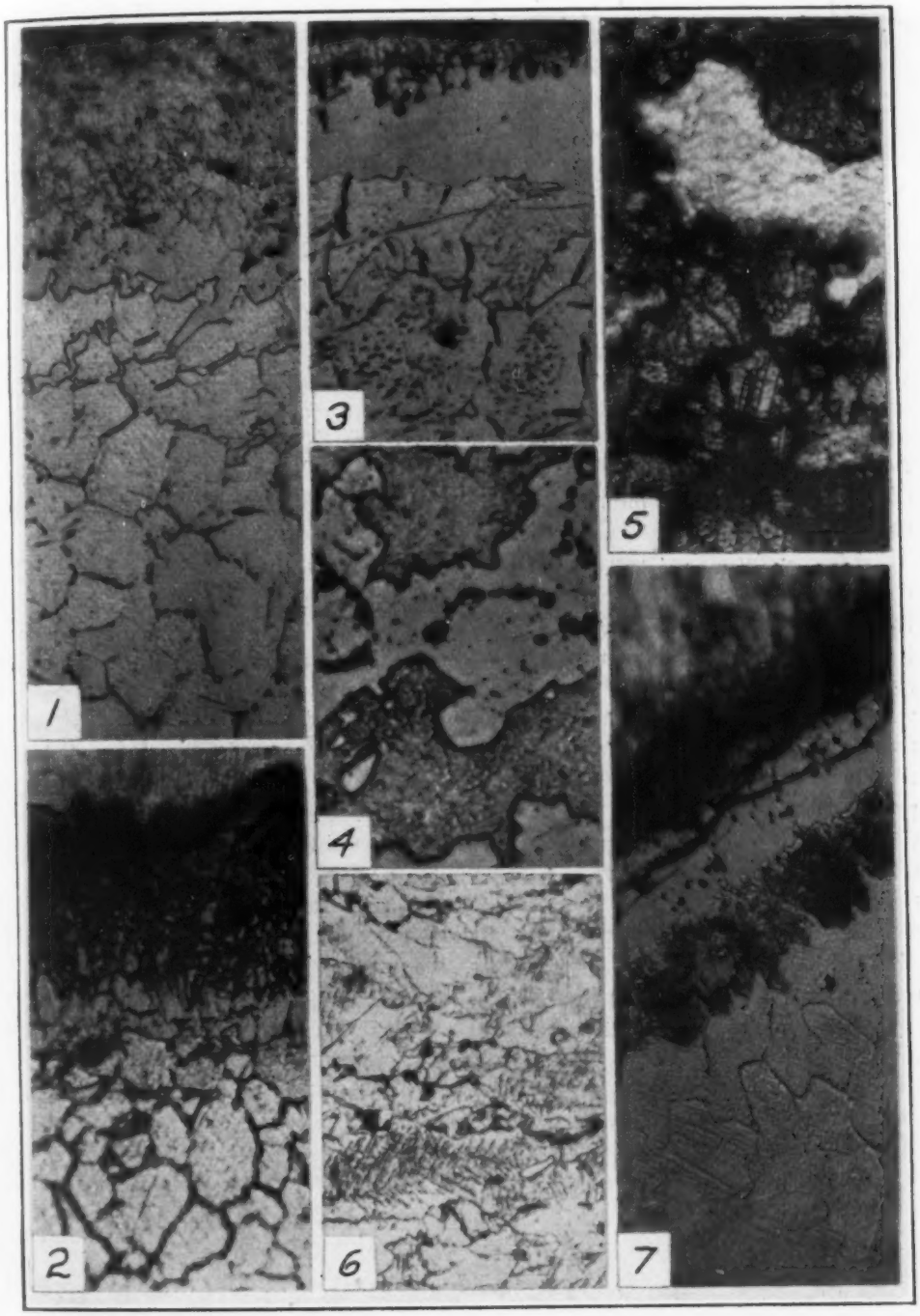

Fig. 1—Edge of Iron Nail (Top) Nitrided to Form Epsilon Phase. Nitric Etch. × 500. Fig. 2—Edge of Iron Nail (Top) Nitrided to Form Epsilon Phase. Prolonged Picric Acid Etch (Extreme Top Shows Solder). × 500. Fig. 3—Edge of Open-Hearth Iron Nitrided to Form Epsilon Phase. Nitric Etch. ×500. Fig. 4—Interior of Electrolytic Iron Block Nitrided to Form Epsilon Phase. Light, Nitric Acid Etch. × 500. Fig. 5—Same as Fig. 4. Deeply Etched with Picric and Nitric Acids. Oblique Illumination. The smooth areas are broken into smaller crystals which show twin bands. The mottled area is dissolved away. × 500. Fig. 6—Interior of Electrolytic Iron Block, Nitrided to Form Epsilon Phase. Deeply Etched with Picric and Nitric Acids. × 500. Fig. 7—Edge of Open-hearth Iron Nitrided to Form Gamma Prime Phase. Nitric Etch. Between the Gamma Prime Phase on Outside and Iron Core is Layer of Braunite. × 250.

longed etching with picric acid. Fig. 3 is a transverse view of the outside case on open-hearth iron. The case is around 0.0014-inch thick. It is clearly indicated that the path of penetration of the nitriding gas is along grain boundaries from whence it must diffuse into the iron crystals. Electrolytic iron blocks were badly warped upon nitriding and upon metallographic examination were found to be badly pitted and heterogeneous in character. In the interior, a stratum was found of which Fig. 4 is representative. The black areas are pits, the smooth white background is of nitrided iron and the mottled area is believed to be alpha iron. The background is broken up by further etching into much smaller crystals showing twinned structure characteristic of gamma prime as is shown in Fig. 5, where the mottled area is shown as a pit. These areas in Fig. 4 are similar to those shown in Fig. 11 of the paper in which the groundmass is designated as alpha iron and the lighter appearing microstructure which appears in relief as Fe_4N. Comparison with Figs. 10 and 12 of the paper leads the present author to believe that the reverse is true and that gamma prime constitutes the background. Fig. 6 shows the microstructure of another area in the interior of the nitrided electrolytic iron block after deep etching.

Similar specimens were annealed at 640 degrees Cent. and nitrided at 572 degrees Cent. $\pm$ 10 degrees for 163 hours in $N_2 - 3H_2 - NH_4$ gas mixture in which the percentage ammonia in the entering gas was 20 $\pm$ 5 per cent thus favoring the formation of gamma prime. The nitrided powder was shown to be Fe_4N by X-ray analyses. The block of electrolytic iron was again badly warped and full of pits. The cylinder of open-hearth iron had two layers formed as shown in Fig. 7, an outer one of gamma prime, 0.0016-inch deep, so brittle that it could be lost when polishing for microscopic examination unless properly protected by solder, and an inner one of Braunite. The temperature of nitriding tended to run high at the latter part of the exposure and indicates that the eutectoid horizontal is near 580 degrees Cent. The gamma prime phase was also to be found at the grain boundaries. Comparatively few nitride needles were to be found within the crystals at the core upon further etching.

This work indicates that the purity of the metal affects the depth of cases, and it seems that the higher the carbon the greater the depth. Figs. 10 and 11 of the paper tend to support this conclusion also. Examination of 3 shows that taking off a cut 0.0031 inches deep would completely remove the case and leave nothing but nitride needles and gamma prime at grain boundaries as is found in Fig. 10. Furthermore, the correctness of Eisenhut and Kaupp's diagram of the iron-nitrogen system is substantiated, especially with reference to the epsilon and gamma prime heterogeneous field.

Author's Closure

With reference to Mr. Kosting's discussion, we wish to say first that he has made some valuable additions to our paper, and it appears that our results are generally in agreement. The only point on which there seems to be some lack of agreement is with reference to our interpretation of the microstructure of Fig. 11 in particular. Our interpretation of this microstructure was based upon the observation that the light structure in Fig. 11 seemed to stand up in

relief and to have dispersed at a greater depth, as shown in Fig. 12. There may have been some differences in our method of etching, and, finally, we are not positive that we are correct.

With reference to the discussion by J. T. Norton, Jr., we wish to point out first that our method of determining the hardness may not have revealed the true surface hardness of the Armco iron and the S.A.E. 1025 steel, because of the very thin hardened layer. It will be appreciated that even with the 10 kilogram load, the Vickers type of indenter may break through an extremely thin case and register more nearly the hardness of the material below the case. It is well known that the large Brinell instrument does not give a true indication of the hardness of thin nitrided cases. The microcharacter might be a better instrument to use in determining the hardnesses of such cases.

Our investigation has yielded practically nothing regarding the mechanism of hardening alpha iron by nitriding. More precise X-ray work may show something with reference to the distortion of the alpha iron lattice, or in some way indicate that nitrogen is present in the lattice. On the other hand careful work at high magnification may reveal under the metallurgical microscope some precipitation phases in these nitrided cases. It is quite within the range of possibility that precipitation phases may exist in such finely divided state that they would not yield an X-ray diffraction pattern.

As I have just indicated, the most likely mechanism for the hardening of these nitrided alpha irons are:

1. The presence of stranger atoms, in this case nitrogen, in the iron lattice, and
2. The presence of a second phase, which in this case would presumably be some form of nitride.

The work by Herbert shows only a slight decrease in hardness when tested at elevated temperatures, until a temperature of 400 degrees Cent. is exceeded. This would suggest that there was no decrease in the hardness due to the solution of a phase at temperatures not exceeding 400 degrees Cent.

With reference to Prof. John T. Norton's discussion, we should explain first that our work was completed in May, 1930, and therefore the paper by Eisenhut and Kaupp had not become available.

Prof. Norton has made some valuable suggestions, and it is to be hoped that either his laboratory or others will continue the work along the line which he has suggested. We feel that more precise work along the line which we have used may possibly yield additional information regarding the effect of various alloying elements, such as chromium, aluminum, molybdenum, and vanadium in producing the extreme hardness observed in nitrided cases.

EVOLUTION OF THE IRON-OXYGEN CONSTITUTIONAL DIAGRAM

By C. H. Mathewson, E. Spire and W. E. Milligan

Abstract

This paper presents a discussion of the constitutional data on iron-oxygen alloys now available, with particular reference to the previous discussion of the same subject by Benedicks and Löfquist. Much attention has been devoted to the question of the composition of the oxide phase in equilibrium with molten iron (containing oxide) and its subsequent change on cooling. The part of the diagram representing equilibrium between a ferrous and a ferric constituent [FeO (approx.) and Fe_3O_4] has been worked out for the first time by the customary thermal and microscopic methods.

As a conclusion of general interest, it may be stated that the oxide phase ordinarily found distributed in the form of small globular inclusions in oxidized iron will occur either in the ferrous or combined ferrous and ferric condition depending upon the thermal treatment.

ABOUT three years ago Benedicks and Löfquist (1)[1] published a complete constitutional diagram of the system Iron-Oxygen taking into account the results of all chemical or metallurgical investigations known to them in which various aspects of the equilibrium between known phases in this system have been presented. Standing at the head of this miscellaneous assortment of detached observations and virtually constituting the point of departure in constructing the diagram was Tritton and Hanson's (2) well known communication of 1924 in which certain essentials of equilibrium between iron and the neighboring oxide phase were set forth.

The diagram of Benedicks and Löfquist is reproduced in Fig. 1 and the purpose of the present communication is to reconstruct it in the light of additional evidence, including some independent verification of important points affecting particularly the equilibrium in

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

From a part of a dissertation to be presented by E. Spire to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Dr. C. H. Mathewson is a member of the society and is Professor of Metallurgy, E. Spire is a graduate student in the department of mining and metallurgy and W. E. Milligan is Assistant Professor of Metallurgy at Yale University. Manuscript received Feb. 13, 1931.

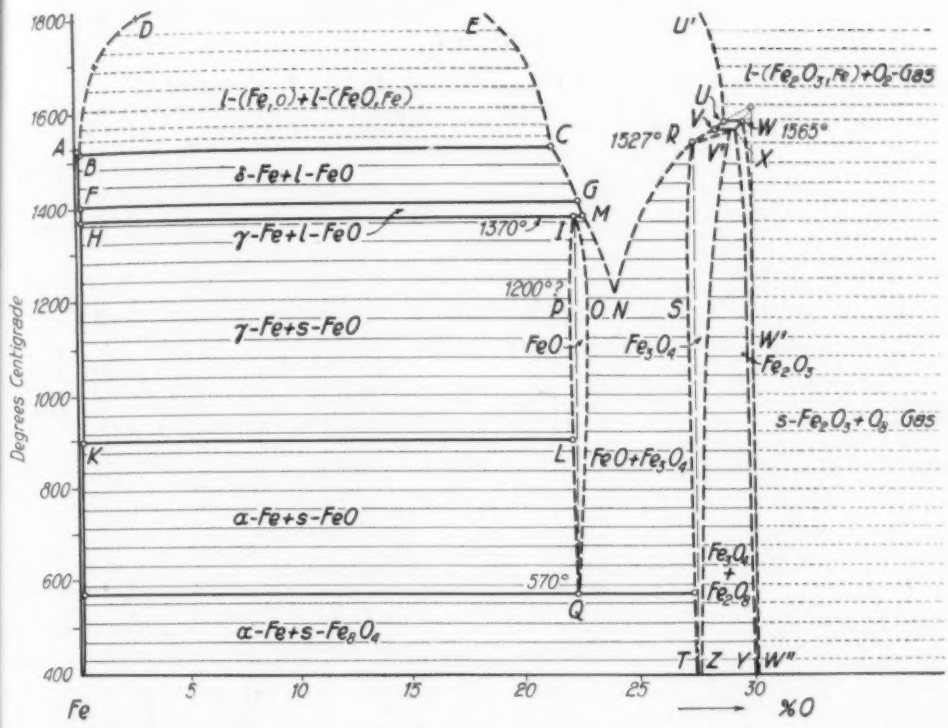

Fig. 1—Fe-O Constitutional Diagram According to Benedicks and Löfquist.

mixtures in which nearly pure iron appears as the predominant phase.

First of all, the location of the biliquidal region BDEC is based upon Tritton and Hanson's analyses of the two layers B and C in equilibrium with the solid phase, δ iron saturated with oxygen, and two points between B and D, attributed to de Coussergues (3), showing the saturation concentrations of oxygen in liquid iron at 1700 and 1800 degrees Cent. De Coussergues, however, obtained these values from a curve published by Eichoff (4) and examination of the reference cited, as pointed out by Herty (5), shows no experimental foundation for the solubility values given. In place of these fictitious values, however, we now have reliable data on the solubility of oxygen in iron at temperatures up to 1734 degrees Cent. communicated by Herty (5) and co-workers. Some of these values are shown in Table I (a) and plotted in Fig. 2.

They represent analytical determinations of the oxygen contained in samples of iron taken at the various temperatures from underneath a slag composed principally of ferrous oxide containing up to approximately 18 per cent of ferric oxide. Since no determinations of free iron were made in these slags no points on Benedicks

Table I

(a)
Solubility of Oxygen in Liquid Iron, Herty and Collaborators (5)

Temperature Melting Point	Oxygen Dissolved 0.21 Per Cent
1600° C	0.304
1700° C	0.452
1734° C	0.552

(b)
Beginning and End of Freezing: Transformation Points, Tritton and Hanson (2)

Oxygen by Analysis	Liquidus Point on Cooling	Oxide Point on Heating	Transformation Points*					
			Ar_4	Ac_4	Ar_3	Ac_3	Ar_2	Ac_2
0.1	1529° C	(1371)	1408 (1396)	(1407)	845		764	(763)
0.12	1525		1394		847 (885)	(912)	759 (763)	(767)
0.15	1526		1394		865 (885)	(912)	764 (763)	
0.18	1526		1394		861		759	(763)
0.21	1519	(1376)	1376 (1396)	(1407)	861 (889)	(912)	751 (763)	

*Values enclosed in brackets determined with particular care in separate experiments not complicated by melting and solidification of the specimen; the A_2 and A_3 points in vacuum. The results indicate no change in the transformation points due to oxygen in this range of concentration. The oxide arrest was checked by experiments on iron containing a quantity of oxide in drilled holes and on iron oxide melted in an iron pot. The former gave 1371 degrees Cent. on heating and 1361 degrees Cent. on cooling; the latter 1371 degrees Cent. on heating and 1369 degrees Cent. on cooling.

(c)
Composition at the Phase Boundaries of Wustite (FeO Solid Solution) and Oxoferrite (Fe Solid Solution) Schenck and Others (16)

Temperature	Per Cent O in Wustite* (a)	(b)	Per Cent O in Oxoferrite
600° C	23.11	24.24	...
650	23.17	24.29	...
700	23.06	24.35	...
800	22.95	24.35	0.4
900	22.84	24.51	...
1000	22.79	24.62	0.4
1100	22.67	24.78	...

*Eutectoid point given as 24 per cent at 560 degrees Cent.

Krings and Kempkens (8) give 0.095 ± .01 per cent oxygen at 800 degrees Cent. and 0.11 ± 0.015 at 715 degrees Cent. for solubility of oxygen in iron; Tritton and Hanson (2) give 0.05 per cent as an approximate figure.

(d)
Thermal Data on System $FeO—Fe_3O_4$

No.	Composition Expressed in Per Cent Oxygen (a) As Weighed In	(b) By Analysis	Beginning of Primary Freezing	Eutectic Freezing	Notes
1	25.7	25.9	1308° C	1170° C	
2	24.9	25.3	....	1170	Primary freezing not detected.
3	24.0	24.6	1270	1165	Eutectic could not be absorbed by annealing in vacuum at 1100° C.
4	24.5	24.4			Cooling curve not obtained. Shows primary FeO solution + Eutectic.
5	23.7	23.9	1300	....	No eutectic visible. Primary freezing over wide temperature range.
6	23.2	....	1340	....	No eutectic. Composition probably approximates 23.5 per cent O. Not verified by analysis. End of primary freezing vicinity of 1220° C.

Ave. composition of eutectic between FeO solid solution and Fe_3O_4 solid solution by measurement of areas in No. 2 (see p. 78) 25.0.

(e)
Miscellaneous Observations

Melting Point of Fe_3O_4 1527° Cent.
Decomposition Point of Fe_2O_3 1565° Cent. } Hilpert and Kohlmeyer (17)

Solid solubility between Fe_2O_3 and Fe_3O_4 at 1150 or 1200 degrees Cent. Ruer and Nakomoto (6)

Fe_3O_4 in Fe_2O_3, inappreciable.

Fe_2O_3 in Fe_3O_4, approx. 2 per cent, (corresponding to concentration of 27.68 per cent O.)

and Löfquist's curve, CE, came out of this investigation, nor have such points been determined elsewhere as far as the authors have been able to learn.

There is little doubt that the location of the point B at 0.21 per cent oxygen by Tritton and Hanson is substantially correct as much confirmatory evidence can be cited. Cf. in this connection Herty's discussion of the available data on page 7 of the paper already cited. The location of the point C at the right hand extremity of the monotectic horizontal is, however, subject to considerable uncertainty. Benedicks and Löfquist in locating this point apparently agree with Tritton and Hanson in the general assumption that this liquid layer normally contains less oxygen than corresponds to the formula, FeO, although they carry the curve CGM, along which the iron phase separates, into the region of solid solutions (between FeO and Fe_3O_4) instead of terminating it at the concentration of pure FeO as was done provisionally by Tritton and Hanson. According to the analysis reported 80.6 per cent of the frozen oxide layer is FeO, 14.0 per cent Fe_2O_3 and 0.99 per cent free iron, with 3.0 per cent of MgO and 0.4 per cent SiO_2 present as impurities. Microscopically, the "free iron" was observed in the grain boundaries of the oxide phase which may be assumed to be solid solution of oxide molecules containing ferrous and ferric iron, presumably FeO and Fe_3O_4.

In plotting points on a binary diagram from these data it would appear essential to subtract the total amount of impurities and calculate the oxygen concentration of point C from the proportions of FeO, Fe_2O_3 and Fe shown in the analysis; likewise the concentration of the point M from the proportions of FeO and Fe_2O_3, the free iron, having separated on cooling to this point. This procedure would locate C at approximately 23.1 per cent O and M at approximately 23.4 per cent O, the compound FeO requiring approximately 22.2 per cent O.

This runs counter to the common assumption that liquid iron at the surface of contact with the oxide phase reduces ferric oxide completely to ferrous oxide while reoxidation occurs at the gas surface owing to the extremely low oxygen pressure of ferrous oxide or even the magnetic oxide.[2] Whitely (9), discussing Tritton and

[2]Ruer and Nakamoto (6) by allowing the products of dissociation of ferric oxide to come to equilibrium at various temperatures in a moving atmosphere of purified nitrogen brought about melting at 1550 degrees Cent. at which point the product had become converted into a mixture of Fe_3O_4 containing 4 per cent FeO. The oxygen pressure of such

Hanson's results cited his own experiments (10) in support of the contention that the reaction $Fe_2O_3 + Fe = 3FeO$ reaches an equilibrium in the oxide phase at 1300 to 1400 degrees Cent. corresponding to the presence of about 8 per cent of ferric oxide in the mixture. This result was obtained by heating oxide originally containing 26 per cent of ferric oxide together with some electrolytic iron sheet in a plugged steel cylinder contained in an evacuated silica tube. Heating for various periods at 1300 to 1400 degrees Cent. with different amounts of ferric oxide always gave approximately the same result. Assuming no free iron in the material, this percentage of ferric oxide corresponds to an oxygen content of about 22.8 per cent oxygen, which is approximately the concentration of the point M as located provisionally by Benedicks and Löfquist to account for the apparent absence of an eutectic point between iron oxide and iron and the failure of all observers to obtain ferrous oxide unaccompanied by coarsely precipitated iron from melts in this region.

In order to obtain first hand evidence concerning the location of the points C and M, samples of iron oxide made by burning electrolytic iron[3] in an oxyhydrogen flame were melted in crucibles prepared from electrolytic iron. At first the crucible containing the oxide was placed inside of a high frequency coil and heated just to the melting point of the iron with rather free access of air. Shortly after the oxide had frozen the crucible was quenched in water. Two melts prepared in this way gave the following results:

		Per Cent Free Iron	Per Cent FeO	Per Cent Fe_2O_3	Calculated Per Cent Oxygen
(1)		1.79	86.08	11.21	22.54
(2)	A-200 mesh	2.25	86.38	11.09	22.54
	B-280 mesh	1.77	87.63	10.85	22.48

Some of the methods recommended by Oberhoffer and Groebler (11) were used in this analysis, viz., free iron was determined by extraction with mercuric chloride, and ferrous iron by the Zimmerman-

a mixture at its melting point is therefore scarcely noticeable and the oxygen pressure of mixtures within the range of the present experiments would be even less. Sosman and Hostetter (7) give the oxygen pressure of Fe_3O_4 at 1200 degrees Cent. as 0.04 mm. Krings and Kempkens (8) in determining the composition of solid solutions of oxygen in iron at 715 and 800 degrees Cent. by bringing them into equilibrium with various mixtures of hydrogen and water vapor, thus indirectly determined the oxygen pressure of iron saturated with FeO (corresponding to 0.08 to 0.125 per cent O) through the medium of the equation $2\ H_2O = 2H_2 + O_2$. Under these conditions the oxygen pressure of the saturated solid solution was of the order of 10^{-21} Atm.

[3]Analysis of this material: (Courtesy of Jerome Strauss, Vanadium Corporation of America): C, 0.035 per cent; P, 0.005 per cent; S, 0.007 per cent; Si, 0.008 per cent. The material was further purified by treatment in hydrogen and in vacuum. No carbide or oxide-sulphide eutectic could be found in the final product.

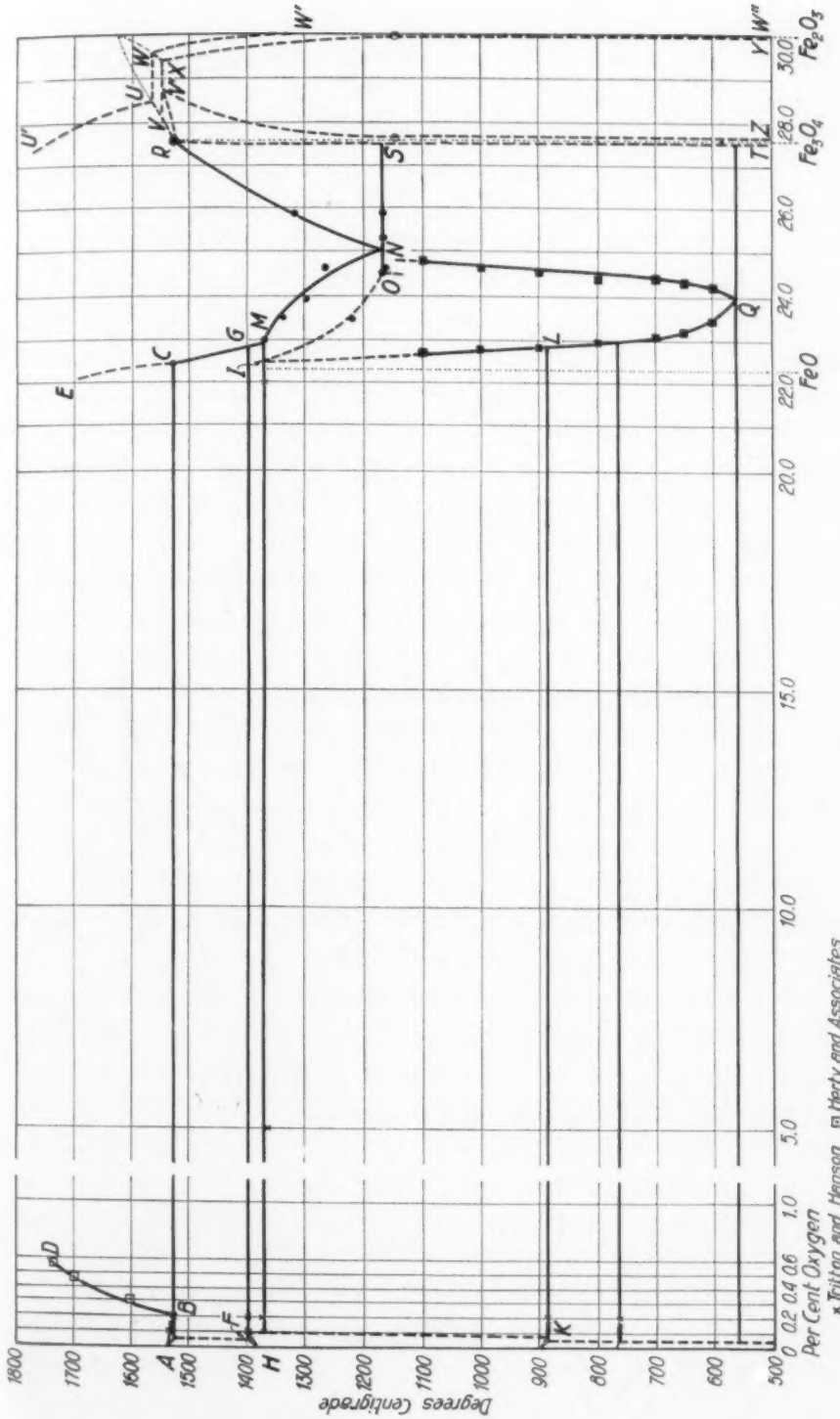

Fig. 2—Revised Iron-Oxygen Constitutional Diagram.

Reinhardt method but ferric iron was found by difference after determining total iron. The details of these procedures are given in an appendix.

It is observed that the oxygen content of these melts is not greatly different from the oxygen content of Tritton and Hanson's oxide layer. Considerably more free iron was found, however, and the reason for this became evident on microscopic examination of sections through the slag and metal. Oxidation of the metal by transfer of oxygen through the slag had proceeded irregularly so as to form detached rounded particles which became part of the oxide mass and could not be separated analytically from the smaller particles of free iron which had precipitated on cooling from C to M.

Photomicrographs of similar preparations have been published by others, notably Wohrman (12), who offers a brief structural diagnosis of the process of oxidation.

In order to avoid abnormal structures due to excessive oxidation, viz., to maintain an approximate equilibrium concentration of the oxide phase in contact with iron at its melting point, a similar experiment was conducted in the virtual absence of oxygen by enclosing the iron crucible in a quartz tube and evacuating to a pressure of less than 1 millimeter. Although the oxygen pressure (of approximately $\frac{1}{5}$ millimeter) is considerably above the dissociation pressure of all oxide mixtures in this range of concentration, oxidation at the surface would probably be slow and the mixture as a whole may confidently be expected to yield approximately the oxygen content of a final reduction product in contact with iron.

It was believed that quenching of the mixture after cooling to a temperature just below the melting point of the oxide would suppress all changes below this point, such as precipitation of iron from solid solution and the final eutectoid transformation of the FeO solution into iron and magnetic oxide at Q, thus making it possible to determine the concentration of point C and that of point M from the analytical results expressed in terms of free iron, ferrous oxide and ferric oxide.

Thus, the total oxygen expressed as a percentage of the total weight of free iron, ferrous oxide and ferric oxide would represent point C and the total oxygen expressed as a percentage of the total weight less the weight of the free iron would represent the point M.

In spite of the precautions taken, microscopic examination again

revealed the presence of large particles of iron in the oxide phase accompanying the much smaller particles of precipitated iron. Figs. 3, 4 and 5 represent this structure and indicate the possibility of removing the large particles by screening before making an analysis to determine the true composition of the mixture of oxide and iron originally held in liquid solution. Comparisons on the camera screen of the microstructure at different locations with similar projected images of various available wire screens led us to believe that a screen showing an aperture of .04 mm. would retain most of the 'detached' iron and pass all of the precipitated particles. The samples were accordingly finely pulverized in an agate mortar and sifted through this (280 mesh) screen.

The results of the analysis of an oxide which had been completely removed from one half of a longitudinal section through the iron container and carefully sampled are given below on the first line. The number (1) refers to an experiment in which the maximum temperature reached was 35 degrees Cent. below the melting point of the iron as nearly as could be determined by means of a simple and convenient optical pyrometer previously calibrated by observing the melting points of the oxide and the iron in vacuum under similar conditions. The number (2) refers to another experiment in which the maximum temperature reached was 23 degrees Cent. below the melting point of the iron and in this case the oxide used in the analysis was removed with a piercing tool so as to preserve the crucible for the other experiment. In both cases the crucible and contents were allowed to cool rapidly in vacuum (150 degrees per minute) until the oxide had frozen, then more rapidly by admitting air and quenching in water as soon as possible. This active quenching occurred at a bright cherry red heat.

	Per Cent Free Iron	Per Cent FeO	Per Cent Fe_2O_3	Calc. Per Cent Oxygen Point C	Calc. Per Cent Oxygen Point M
(1)	2.20	89.11	8.41	22.43	23.00
(2)[4]	2.20	87.91	7.91	22.10	23.06

Although the above method of eliminating iron properly belonging to the metal phase can not be considered strictly accurate it is noteworthy that identical results have come from the two experiments. This percentage of free iron (2.20) is considerably greater

[4]The sum of the free iron, ferrous oxide and ferric oxide in sample (2) falls about 2 per cent short of 100, probably owing to a small amount of foreign material (insoluble residue) in this sample.

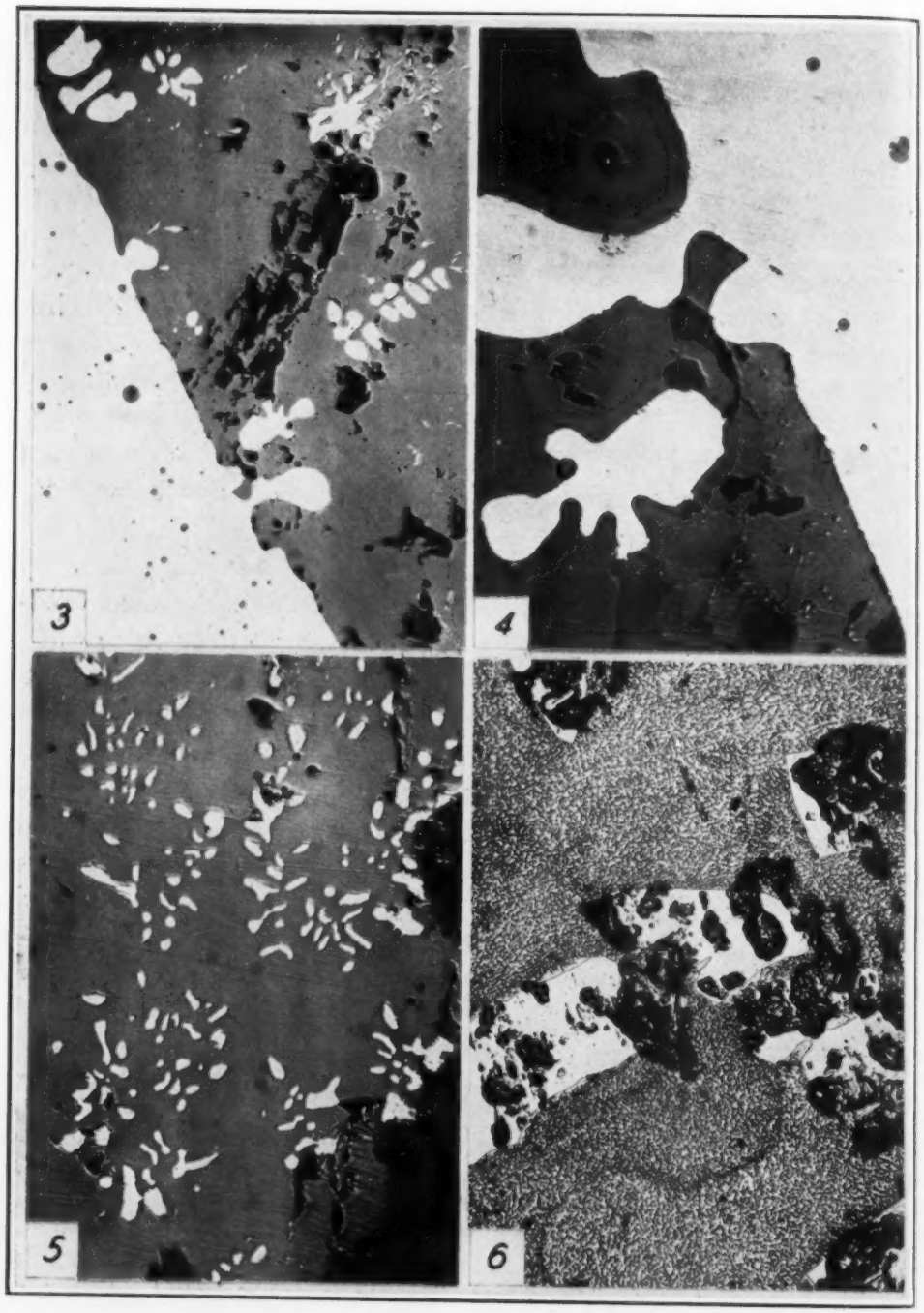

Fig. 3—Photomicrograph Showing Large and Small Particles of Iron in the Oxide Phase. × 75. Fig. 4—Large Particles of Iron at Boundary Showing Manner of Formation. × 250. Fig. 5—Precipitated Particles of Iron. × 250. Fig. 6—Preparation Containing 25.3 Per Cent O (No. 2, Table 1 (d) Showing primary Fe_3O_4(Fe) and Eutectic of Fe_3O_4(Fe) + FeO(O). × 75.

than the value (1 per cent) obtained by Tritton and Hanson who analyzed a sample which had been in contact with liquid iron but contained about 3 per cent of magnesia and some silica absorbed from the crucible. There is obviously some doubt as to the true conditions but we have used our own data (2.20 per cent O) in plotting the point C of Fig. 2, which therefore represents an oxide melt very closely approximating the composition of pure FeO.

We have considerable confidence in the method used for extracting free iron from the oxide (Groebler and Oberhoffer, 11) and believe that the true oxygen concentration of point M, obtained by calculating the percentage of oxygen in the material remaining after removing the free iron, is very close to 23 per cent, viz., perceptibly greater than the oxygen content of pure FeO (22.27). This indicates that the interpretation of the reaction at 1370 degrees Cent. by Benedicks and Löfquist is correct, viz., that the line HIM of Fig. 1 is a peritectic horizontal. The revised data are plotted in Fig. 2 where is appears that this reaction between liquid of concentration M and solid of concentration H must result in a solid of concentration I, 22.5 per cent O, which closely approximates the composition of pure FeO. The solid solubility data of Schenck and his collaborators (16) (curve IQ) were used in provisionally locating the point I.

It was expected that microscopic examination of the rapidly cooled sample No. 1 (described on p. 73) after high temperature annealing in vacuum would show signs of a reaction between the oxide solution and the precipitated iron but the original structure persisted after annealing 30 minutes at 1200 degrees Cent. and it could not be concluded that any of the finely divided precipitated iron (shown in Fig. 5) had dissolved. It is of course possible that the peritectic reaction occurred during the rapid cooling of the specimen, in which case, the analytical procedure (p. 72) used to determine point M would be incorrect and the value obtained would in reality refer to point I. In any event, these two points must lie very close together and their exact location will inevitably be difficult.

On the basis of these results the dotted line CM of Benedicks and Löfquist's diagram (Fig. 1) has been replaced by a definitive line CM in the modified diagram (Fig. 2).

Benedicks and Löfquist's diagram between M and R, the freezing point of the magnetic oxide, is mainly hypothetical, based solely on the qualitative observation of a eutectic structure in certain mix-

tures of rather indefinite composition in this general region. Wyckoff and Crittenden (13) reported that microscopic examination of a preparation showing by analysis 3.34 per cent free iron, 40.49 per cent ferrous iron and 31.41 per cent ferric iron, although perhaps containing much less ferric iron than this, revealed "large crystals of ferro ferric oxide embedded in a fine grained eutectic mixture of magnetite and another phase which is presumably ferrous oxide." The examination was made on a polished section heated to dull redness. "Magnetite is unchanged by this treatment but the surface of the FeO grains becomes matte." No photomicrograph was published. Assuming the analysis to be correct in the face of the skepticism of the authors, and neglecting the presence of free iron, a mixture of FeO and Fe_3O_4 containing about 25.8 per cent oxygen, this representing about 32 per cent of FeO, is therefore located on the Fe_3O_4 side of the hypothetical eutectic.

Oberhoffer and d'Huart (14) have published micrographs (low and high magnification) showing an eutectic network of incompletely identified oxides accompanied by iron in a sample of oxide melted in an iron crucible but not analyzed. A light colored primary constituent, present in excess, is presumed to be a solid solution based upon Fe_3O_4 and the eutectic is composed of this light constituent associated with a much greater amount, perhaps 85 to 90 per cent, of a dark constituent, presumed to be a solid solution based upon FeO.

A cooling curve of another sample of oxide (prepared by burning iron in air) taken with a bare thermocouple in a platinum crucible gave a definite arrest at 1450 degrees Cent. (presumably the primary freezing point) followed by inflections at 1200 and 1020 degrees Cent. The 1200-degree point was provisionally selected by Benedicks and Löfquist as the eutectic temperature. In evaluating these piecemeal data, it must be observed that the solid solubility at the left hand extremity of the eutectic point N has been shown by Schenck and co-workers (15, 16) to be much more extensive than is indicated in Fig. 1. Their data which are reproduced in Table I (c) give equilibrium concentrations at temperatures up to 1100 degrees Cent., i.e., reasonably close to the eutectic temperature in question, and at this point the saturation concentration of the ferric oxide in ferrous oxide is reported as 24.78 per cent oxygen. The same authors, in agreement with Wyckoff and Crittenden (13) find no solid solubility of ferrous oxide in ferric oxide. Others, notably

Groebler and Oberhoffer (11) report a small solubility obviously less than 4.6 per cent (corresponding to about 27.4 per cent O) at 800 degrees Cent. in this region. A hypothetical eutectic located at 25.2 per cent O with its structural components at 24.8 and 27.4 per cent O, respectively, would contain approximately 85 per cent of the former (ferrous phase). This represents about the best interpretation that can be put upon the available data.

In order to more completely explore this portion of the diagram a number of mixtures, Table I (d), were prepared by melting together in vacuum in a platinum crucible various proportions of (1) an oxide previously prepared by burning iron in oxygen and comparatively high in ferrous oxide (23.2 per cent O) and (2) another high in magnetic oxide (25.7 per cent O) obtained by igniting the former in air at 800 degrees Cent.

In each of these experiments, about 35 grams of material was used. Cooling curves were taken with an unprotected platinum, platinum-rhodium couple after calibration with pure silver and copper. When the temperature had fallen to about 900 degrees Cent. air was let into the heating chamber and the crucible and contents were promptly removed and quenched in water.

The reguli, which could be removed without difficulty from the platinum crucible after quenching, were mounted in tin and sawed in two longitudinally so as to provide one specimen for microscopic examination and a liberal quantity for analysis.

It was considered adequate in this part of the work to obtain the oxygen content by difference after a simple determination of total iron. Samples for analysis were prepared from the quenched material in the customary manner by grinding in an agate mortar. Not more than a trace of free iron (.015 to .022 per cent) could be found in the pulverized material thus proving that the severe mechanical disturbance of fine grinding had no marked tendency to initiate the normal eutectoid transformation in this supercooled solid solution.

The first of these preparations in which two parts of (2) and one part of (1) were used, was found to consist principally of eutectic with a small quantity of primary constituent lighter in color and more resistant to acid attack than the predominant constituent of the eutectic. The latter is therefore the ferrous solid solution, here associated with the magnetic oxide both as a constituent of the eutectic and as a primary structure element.

A micrometric determination of the relative areas occupied by primary constituent and eutectic was made by preparing several micrographs at low magnification, printed through a cover plate bearing an image of coordinate paper, and counting the number of squares occupied by each constituent. One of these micrographs is shown in Fig. 6. The black spots represent cavities which could not be avoided in preparing the section on account of brittleness. In the absence of contrary evidence it was assumed that both constituents were broken away indiscriminately in these regions and the areas in question were accordingly subtracted in making the micrometric determination.

A summary of this determination follows:

Micrograph No.	Per Cent Eutectic
1	88.2
2	87.9
3	85.8
4	85.9
Average	86.9

Assuming the oxygen content of the primary constituent to be 27.4,[5] the eutectic in the above sample, which contains 25.3 per cent of oxygen and shows 86.9 per cent of eutectic by area measurements, would have to contain approximately 25.0 per cent of oxygen if no account were taken of the densities of the two solid solutions. However, the densities of these two constituents[6] are so nearly alike that a correction of this sort merely increases the above figure in the second place beyond the decimal point. Moreover, if the primary constituent is assumed to be pure Fe_3O_4 the changes are mutually corrective and the figure remains at 25.0 per cent of oxygen. It is, of course, possible to calculate the composition of the ferrous constituent of the eutectic by using the above value for the oxygen content of the eutectic in connection with the probable value 27.4, or perhaps 27.6, for the oxygen content of the ferric constituent, and the proportions of the two constituents as obtained from area measurements properly corrected to give the proportion by weight.

Thus, the proportions of ferrous and ferric constituents in the eutectic of Fig. 7 were found to be 80.1 and 19.9 by volume, or 82.2

[5]Cf. p. 76.

[6]Wyckoff in the International Critical Tables, Vol. 1, p. 342 gives 5.99 and 5.21 for the densities of FeO and Fe_3O_4, respectively, but Wyckoff and Crittenden (13) find the length of the edge of the unit cube of FeO increased by about 0.3 to 0.4 per cent in a preparation containing considerable Fe_3O_4.

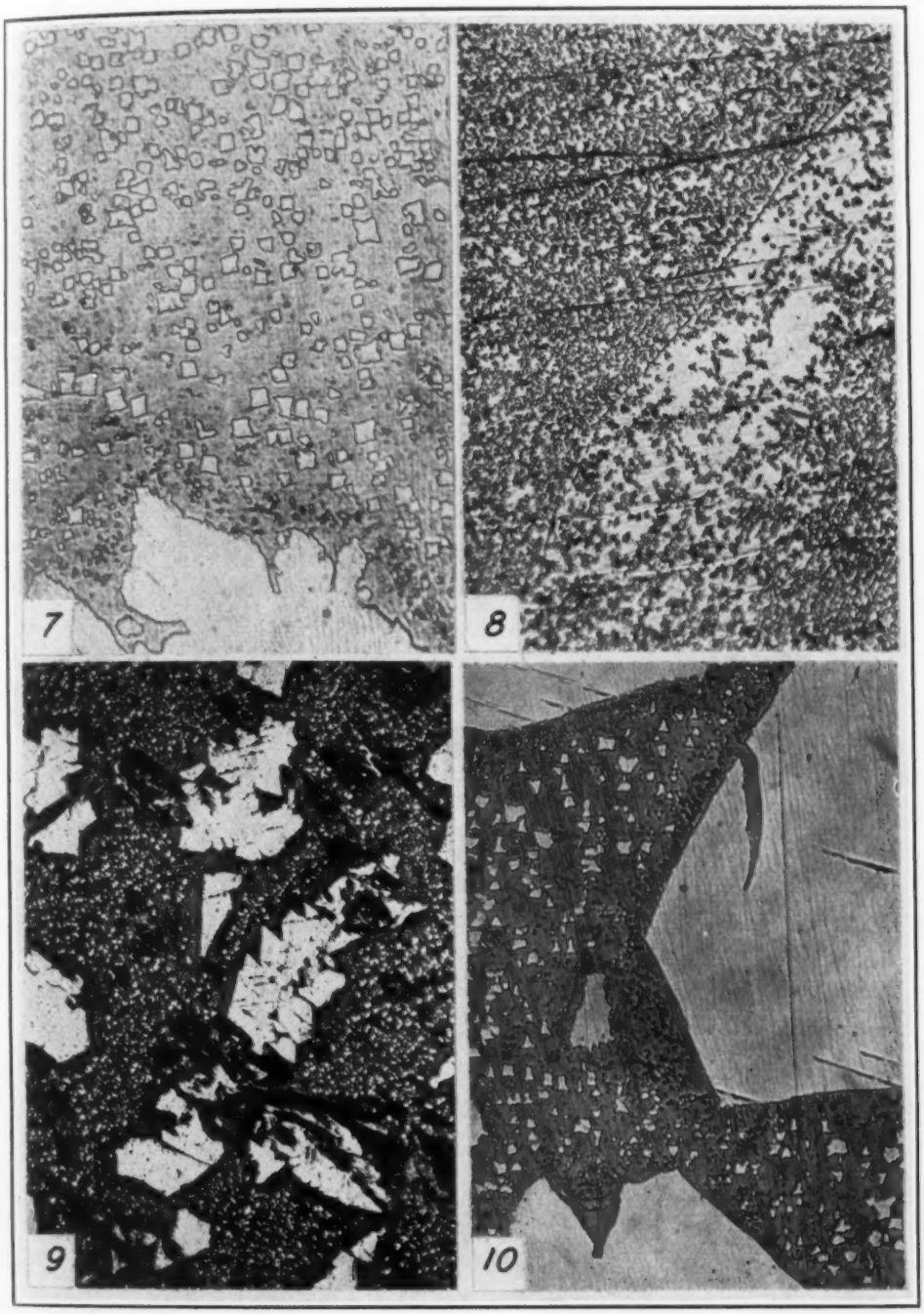

Fig. 7—Photomicrograph Showing Eutectic of Fig. 6. × 750. Fig. 8—Primary FeO(O) and Eutectic in Preparation (No. 4) Containing 24.4 Per Cent O. × 75. Fig. 9—Primary Fe_3O_4(Fe) and Eutectic in Preparation (No. 1) Containing 25.9 Per Cent O. × 75. Fig. 10—Eutectic of Fig. 9. × 500.

and 17.8 respectively by weight. If the oxygen content of the ferric constituent is taken to be 27.4 per cent and that of the eutectic, 25.0, as determined above, the ferrous constituent must contain 24.5 per cent of oxygen, which is 0.3 less than the value given by Schenck[3] for 1100 degrees Cent. Assuming the ferric constituent to be pure Fe_3O_4 (27.64 per cent O) as believed by Schenck and others,[5] the oxygen content of the ferrous constituent decreases still further, to approximately 24.4 per cent.

Further evidence bearing on this point is available from the thermal data given by the other mixtures prepared during the course of this investigation and reported in Table I (d). Thus, a mixture containing 24.6 per cent of oxygen (No. 3) contained a large proportion of eutectic which could not be absorbed by annealing in vacuum at 1100 degrees Cent. Primary ferrous constituent and eutectic are seen in the micrograph (Fig. 8) of a mixture containing 24.4 per cent of oxygen (No. 4). The next preparation in order, No. 2, containing 25.3 per cent of oxygen, lies on the other side of the eutectic concentration and was used for the micrometric determinations (Cf. Figs. 6 and 7) previously described. Preparation No. 1 (Fig. 9) shows a larger proportion of primary Fe_3O_4. Certain portions of the eutectic closely surrounded by the primary constituent in this specimen show very clearly (Fig. 10) the tendency of the latter to divorce the small particles of similar composition from the matrix of ferrous solution.

The other two preparations listed in Table I (d), viz., Nos. 5 and 6 are composed entirely of ferrous solution. Due to their normally homogeneous structure it is easily possible to observe in them the superficial effect of oxidation which occurs at the exposed surface when air is introduced at a cherry red heat just prior to quenching. As represented in Fig. 11, this results in a narrow zone of magnetic oxide at the surface followed by a zone of mixed ferrous and ferric constituents which merges gradually into the main mass of ferrous constituent.

The faulty adjustment between our results and those of Schenck is clearly shown in Fig. 2 where all of the available data have been plotted for comparison and study.

The magnetic oxide, Fe_3O_4, melting point 1527 degrees Cent., according to Hilpert and Kohlmeyer (17) may be taken as the natural end point at the right in this part of the diagram and in con-

formity with the results of X-ray studies by Wyckoff and Crittenden (13) and by Groebler and Oberhoffer (11) the practical absence of solid solubility on the Fe_3O_4 side[7] is indicated by a dotted curve lying close to the Fe_3O_4 vertical at 27.6 per cent O.

The solid solution field IPLQOI of Benedicks and Löfquist's diagram is considerably enlarged in Fig. 2 on the basis of data on the so-called stable system communicated by Schenck, Dingman, Kirscht and Wesselkock (16) and reproduced in Table I (c). In this most recent work of Schenck and his collaborators, following a critical discussion by Benedicks and Löfquist (18) of the errors inherent in the experimental determination of phase boundaries corresponding to significant changes in vapor pressure ("Abbau" curves), the earlier results are revised and brought into more trustworthy form.

The most important changes from the earlier data, however, relate to the concentration of oxygen in the iron phase which is in equilibrium with a corresponding oxide phase of the solid solution field defined above. The unusually high concentration of this phase as determined from considerations of gas equilibria by the earlier investigators, Matsubara (19), Eastman and Evans (20) and confirmed by Schenck and Dingman (15) could not be reconciled with the metallographic results of Tritton and Hanson (2) and gave rise to the well considered criticism of Benedicks and Löfquist, in support of the view that iron can hold only a fraction of a per cent of oxygen in solid solution instead of several per cent as indicated by the changing gas concentration in this region.

More effective measures towards the attainment of true equilibrium in this recent work from Schenck's laboratory has reduced the apparent saturation concentration of oxygen in iron at 800 and 1000 degrees Cent. to the value given in Table I (c) and further attempts in this same direction by Krings and Kempkens (8) have lowered this value still further, viz., to approximately 0.1 per cent oxygen at 800 degrees Cent.

Other observations relative to the solubility of oxygen in iron have been made by A. Wimmer (21) who gives microscopic evidence of the presence of oxide in a carefully analyzed heat of "Flüsseisen" forged at 950 degrees Cent. containing 0.035 per cent oxygen. Many

[7]Wyckoff and Crittenden find no change in the lattice parameter of Fe_3O_4 due to solution of FeO while Groebler and Oberhoffer do find evidence of such a change, but conclude that the solubility cannot be greater than 5 per cent in a preparation brought to equilibrium at 800 degrees Cent.

observations bearing indirectly on the solubility of oxygen in iron might be cited but nothing of precise significance has yet been discovered concerning the trend of the saturation curve with temperature, particularly in relation to the transformation points of iron.

In this connection Benedicks and Löfquist have rejected possibilities put forward by Schönert (22) and by Oberhoffer (23) in favor of the interpretation reproduced in our own Fig. 2 according to which the solubility of oxygen in gamma iron is greater than the solubility in delta or alpha, respectively, the last two possessing the same lattice structure, at the transformation temperature, i.e., oxygen lowers the temperature at which gamma transforms to alpha, regarded by Benedicks and Löfquist as extremely probable,[8] and by analogy raises the temperature at which gamma transforms to delta.

Schenck and Dingman (15) by a method of graphical extrapolation based upon their own experimental data locate the eutectoid point Q at 24 per cent oxygen and 560 degrees Cent. Others, notably Eastman (27), Eastman and Evans (20), and Chaudron (28) have studied the equilibria of the reactions:

$$\left.\begin{array}{l} FeO + H_2 = Fe + H_2O \\ Fe_3O_4 + H_2 = 3FeO + H_2O \end{array}\right\}$$

$$\left.\begin{array}{l} FeO + CO = Fe + CO_2 \\ Fe_3O_4 + CO = 3FeO + CO_2 \end{array}\right\}$$

at different temperatures and by plotting the experimentally determined equilibrium constants of one or the other pair in relation to the temperature have found points of intersection corresponding to coexistence of Fe, FeO and Fe_3O_4, and therefore to the present eutectoid inversion, at temperatures varying from 560 to 580 degrees Cent. The general agreement of all these results is good and the values 24 per cent oxygen and 570 degrees Cent. are therefore used for the point Q in our Fig. 2.

In order to determine the structural condition of the oxide globules in iron and of the accompanying massive oxide phase as affected by prolonged heat treatment above and below the eutectoid point, the specimen used in locating point M (No. 1 described on p. 73) was (a) annealed 40 hours in an evacuated glass tube at 550 degrees Cent. and (b) annealed 16 hours under similar conditions at 650 degrees Cent.

Typical microstructures are shown in Figs. 12, 13, and 14. The

[8]Cf. in this connection Austin (24), Reed (25) and Humfrey (26).

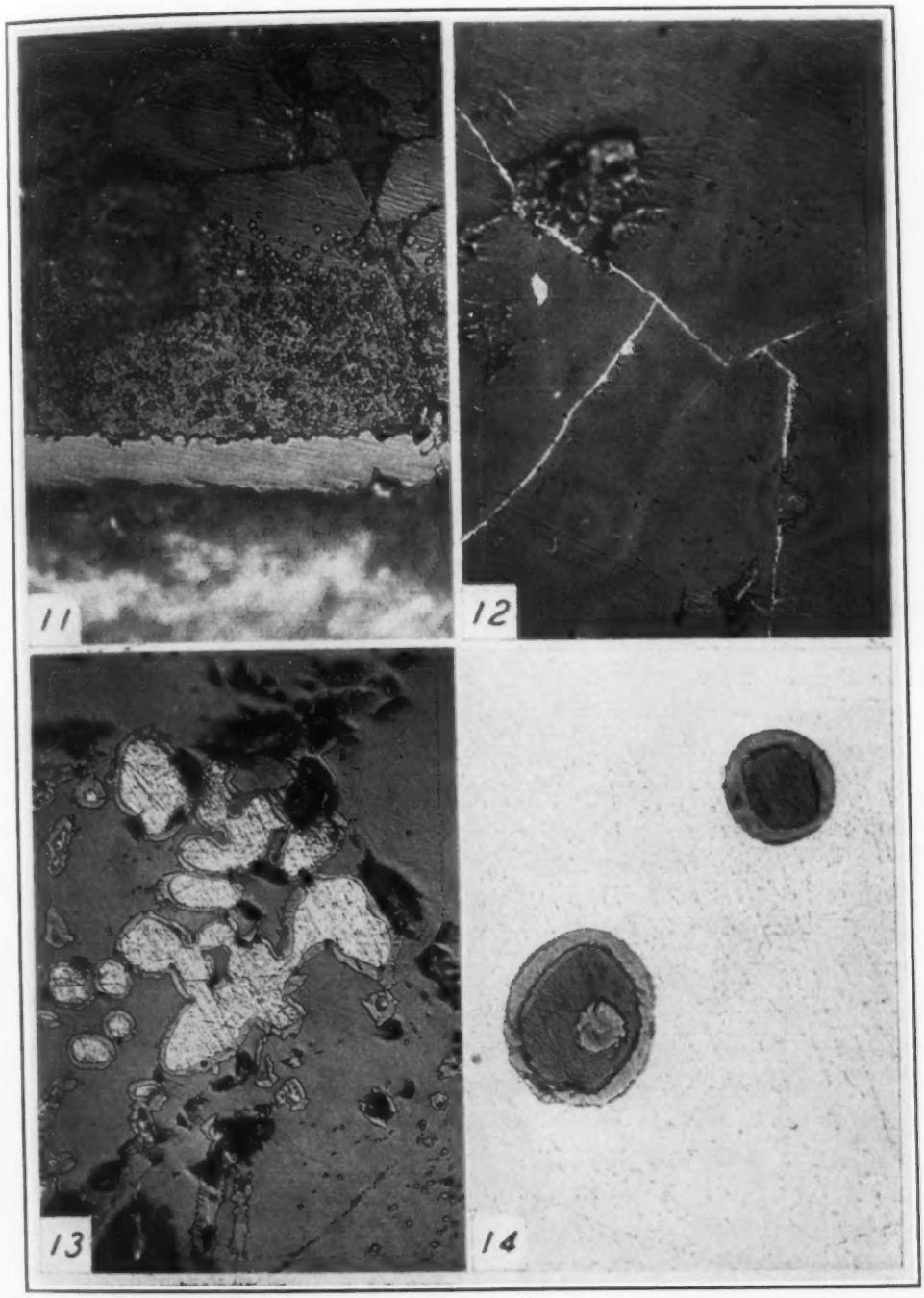

Fig. 11—Photomicrograph Showing Structural Effect of Superficial Oxidation During Cooling of FeO-Fe_3O_4 Mixtures. Surface of No. 5 Containing 23.9 Per Cent O. × 500. Fig. 12—Iron Precipitated by Annealing at 550 Degrees Cent. in Oxide Containing 25.4 Per Cent O. Previously Quenched Immediately After Solidification. Unetched. × 500. Fig. 13—Envelopment of Iron Particles by Magnetic Oxide Fe_3O_4 after Low Temperature Annealing. Etched With 1 Per Cent HCl in Alcohol. × 750. Fig. 14—Structural Change in the Oxide Inclusions of Pure Iron After Annealing Below the Eutectoid Transformation Point. × 1500.

low temperature treament has caused separation of the iron solid solution in the form of small particles and threads or narrow bands as seen in Fig. 12 unetched. On etching with a dilute solution of 1 per cent of HCl in alcohol it is seen, Fig. 13, that the precipitated iron is always enveloped by a structurally clear light colored oxide phase, undoubtedly Fe_3O_4. It would appear that the iron corresponding to decreasing solubility with the temperature along curve IQ separates first from the supercooled solution and then serves as a nucleus for the completion of the transformation. It seems likely that the transformation has occurred in the rest of the material without visible structural separation of the products, this part of the material therefore consisting essentially of magnetic oxide but with about 10 per cent (according to the diagram) of finely divided iron disseminated through it. It will be recalled that etching was required to bring out a difference between this and the material bordering the iron.

Not only the precipitated iron but also the iron present in massive form serves as a nucleus in facilitating the transformation, as may be seen in the case of the large enveloped iron particles of Fig. 13 or indeed the oxide globules of Fig. 14. The latter are the normal oxide inclusions in iron which after slow cooling are quite structureless in pure iron except for specks of free iron occasionally visible in their interior where coalescence with the surrounding massive iron has been avoided.

The effect of the present heat treatment below the transformation temperature has been to produce a border of structurally free magnetic oxide next to the iron, leaving an uncoagulated or possibly untransformed mixture in the interior. One of these globules, shown in Fig. 14, exhibits the usual border and in addition an interior border around a small speck of structurally free iron. Similar conditions were frequently observed.

When a specimen in which the above structures have been developed is reannealed at a temperature above the transformation point (treatment b on p. 82) the borders disappear and the finely divided precipitated iron dissolves completely.

We found this process completely reversible and observed the typical structures described above in samples of oxide melted in iron crucibles either in air or in vacuum.[9]

[9]Chaudron (28) has also observed lamellae of precipitated iron in a sample of ferrous oxide annealed one week at 500 degrees Cent., and also their subsequent disappearance on annealing at 800 degrees Cent. The product of the low temperature anneal was strongly ferro magnetic and "gave a deposit of metal in a solution of copper sulphate."

Between Fe_2O_3 and Fe_3O_4 the oxygen pressure rises sufficiently to materially change the composition of mixtures selected for thermal analysis during the ordinary process of melting and solidification under the normal oxygen pressure of the atmosphere. Nevertheless, Kohlmeyer (29) has utilized complicated data from cooling curves of this character in constructing a constitutional diagram from which it may be argued that several compounds containing higher ratios of Fe_2O_3 to FeO than the 1:1 ratio in Fe_3O_4, form peritectically at various significant temperatures.

In direct contradiction to this, Sosman and Hostetter (7) have observed a continuous change in the oxygen pressure with the composition of mixtures in this range indicating a continuous series of solid solutions at 1100 and 1200 degrees Cent. Benedicks and Löfquist in presenting their diagram disregard the former and reject the latter on the basis that Fe_3O_4 and Fe_2O_3 are unlike in crystal structure and must show a concentration interval of heterogeneous structures. They accept the temperature, 1565 degrees Cent., at which, according to Hilpert and Kohlmeyer (17), Fe_2O_3 powder melts and partially decomposes when rapidly heated, as a decomposition point (equilibrium between O_2 gas at 160 millimeters pressure, liquid solution and Fe_2O_3 (Fe) solid solution), and provisionally assume a peritectic relationship between Fe_2O_3 and Fe_3O_4 at a lower temperature. The solid solubility between Fe_3O_4 and Fe_2O_3 is assumed to be considerable at the peritectic reaction temperature and virtually absent at very low temperatures.

In the absence of more definitive data we have adhered completely to this interpretation in constructing the liquidus and solidus curves in this portion of Fig. 2. The data on solid solubility in the neighborhood of 1200 degrees Cent. given by Ruer and Nakamoto (6) (see Table I e) have been used to define the curves V^1Z and XY (the latter practically coincident with the vertical at Fe_2O_3 in this region).

Analytical Procedures for Determining Metallic Iron, Ferrous Oxide and Ferric Oxide in Materials Prepared During the Course of this Investigation

Metallic iron was determined by the Wilner-Merck method as outlined in Treadwell Hall, 5th Edition (1919), p. 611, and recently recommended by Groebler and Oberhoffer (11). In our own work,

flasks calibrated for 135 cubic centimeters capacity at 14.5 degrees Cent. were used, from which volume 50 cubic centimeters aliquot parts were pipetted. Precautions were taken to have the contents of the flask cooled to 14.5 degrees Cent., after digestion of the sample with mercuric chloride, diluted with water at 14.5 degrees Cent., and the filtrate from which aliquot parts were finally taken brought to the same temperature. Titration of the aliquot portion after dilution, acidification and addition of phosphoric acid—sulphuric acid solution, was made with a standard potassium permanganate solution of strength 0.95 grams $KMnO_4$ per litre. This solution was standardized against iron wire of "analyzed grade."

The determination of total ferrous iron was carried out on a separate sample from which the metallic iron had not been removed. It was considered preferable to analyze the oxides in this manner, notwithstanding the possible reduction of some ferric chloride by hydrogen generated during solution of the metallic iron. In this way, the possibility of oxidizing iron in the supercooled ferrous oxide, during removal of free iron, was avoided.

A possible complication was introduced due to the fact that all oxide samples had been quenched in water and allowed to dry naturally in the air. Drying at 110 to 120 degrees Cent. prior to weighing was not considered advisable because of possible oxidation of the high ferrous oxide mixtures. However, no considerable amount of moisture could have been present, since no great difficulty was experienced with blinding of the extremely fine screen employed during the preparation of the sample.

The well known Zimmerman-Reinhardt method was used in the determination of total ferrous iron. Determinations were carried out on 0.5 gram portions in 300-cubic centimeter Erlenmeyer flasks. The oxide was weighed into the flasks, one gram of C.P. sodium carbonate crystals was added and then 25 cubic centimeters of 1:1 HCl. The flasks were stoppered with a one-hole rubber stopper, through which passed an inverted capillary U-tube, the outer end of which was inserted in a test tube containing a saturated solution of C.P. sodium carbonate. This strength and quantity of acid appeared to be suitable, as solution of the oxide was fairly rapid and the concentration of HCl in the final solution was not too high for accurate titration. When solution was complete, the flask and contents were cooled to tap water temperature, transferred to a 600-cubic centimeter

beaker, diluted to 500 cubic centimeters, 10 cubic centimeters of "Guard solution" added, and titrated. The titration was effected slowly, using a potassium permanganate solution containing 4 grams per litre. Standardization of this solution was made against an amount of iron wire of previously mentioned grade, approximately equivalent to the amount of oxide to be used in the subsequent determination. The standard was dissolved and treated in the same manner and at the same time as the unknown. The conditions of concentration of acid and "Guard solution" were approximately the same in all determinations.

Ferric iron was obtained by difference after determining total iron according to the above method following reduction of all the iron with stannous chloride. This determination was made on 1 gram of material, which was transferred to a 600-cubic centimeter beaker, covered with 25 cubic centimeters of 1:1 HCl, and gently heated. The reduced ferrous chloride solution was titrated with the potassium permanganate solution used in the determination of ferrous iron. Standardization was by means of iron wire treated in the same manner as the unknown.

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DENDRITES IN NICKEL STEEL

By Albert Sauveur and E. L. Reed

Abstract

The paper deals with the action of nickel in promoting persistent dendritic segregation. The dendritic pattern is intensified rather than diminished by long annealing. Quenching in iced brine likewise fails to erase it. In nickel steels which are martensitic after air cooling, but which become pearlitic after long annealing the axes of the dendrites are pearlitic, while the fillings remain martensitic.

SOME alloys of iron and nickel and of iron, carbon and nickel were prepared by melting Armco iron in an Arsem vacuum furnace with the desired amounts of carbon and nickel. The melts were usually held at a temperature of 2200 degrees Fahr. (1205 degrees Cent.) for ten minutes and cooled with the furnace by turning off the power in increments of one kilowatt every 3½ minutes. In 30 minutes the ingots were cooled to a black heat, which was considered a rapid rate of solidification. When lack of homogeneity was suspected, the ingot was remelted under like conditions.

For the purpose of thorough annealing, the samples were heated and cooled in a gas furnace[1] effectively insulated by brick work and asbestos in which they were held for one hour at 1000 degrees Cent. Cooling in this furnace from 1830 to 122 degrees Fahr. (1000 to 50 degrees Cent.) required 60 hours. Decarburizing and oxidizing were prevented by placing the samples in steel tubes with cast iron chips. An alloy containing 0.04 per cent carbon and 9.79 per cent nickel exhibited in the cast and annealed condition the dendritic structure shown in Fig. 1, from which it is inferred that nickel causes dendritic segregation. The fillings of the dendrites are richer in nickel than the axes which permits selective action of the etching reagent.

[1]This furnace is described in E. L. Reed's paper on "Influence of Special Elements on the Iron Carbon-Eutectoid Composition," presented at this meeting.

A paper presented before the Thirteenth Annual Convention of the society, Boston, September 21 to 25, 1931. Of the authors who are members of the society, Dr. Albert Sauveur is Gordon McKay Professor of Metallurgy and Metallography at Harvard University, Cambridge, Mass., and Dr. E. L. Reed is research metallurgist with the American Sheet and Tin Plate Company at Pittsburgh. Manuscript received May 13, 1931.

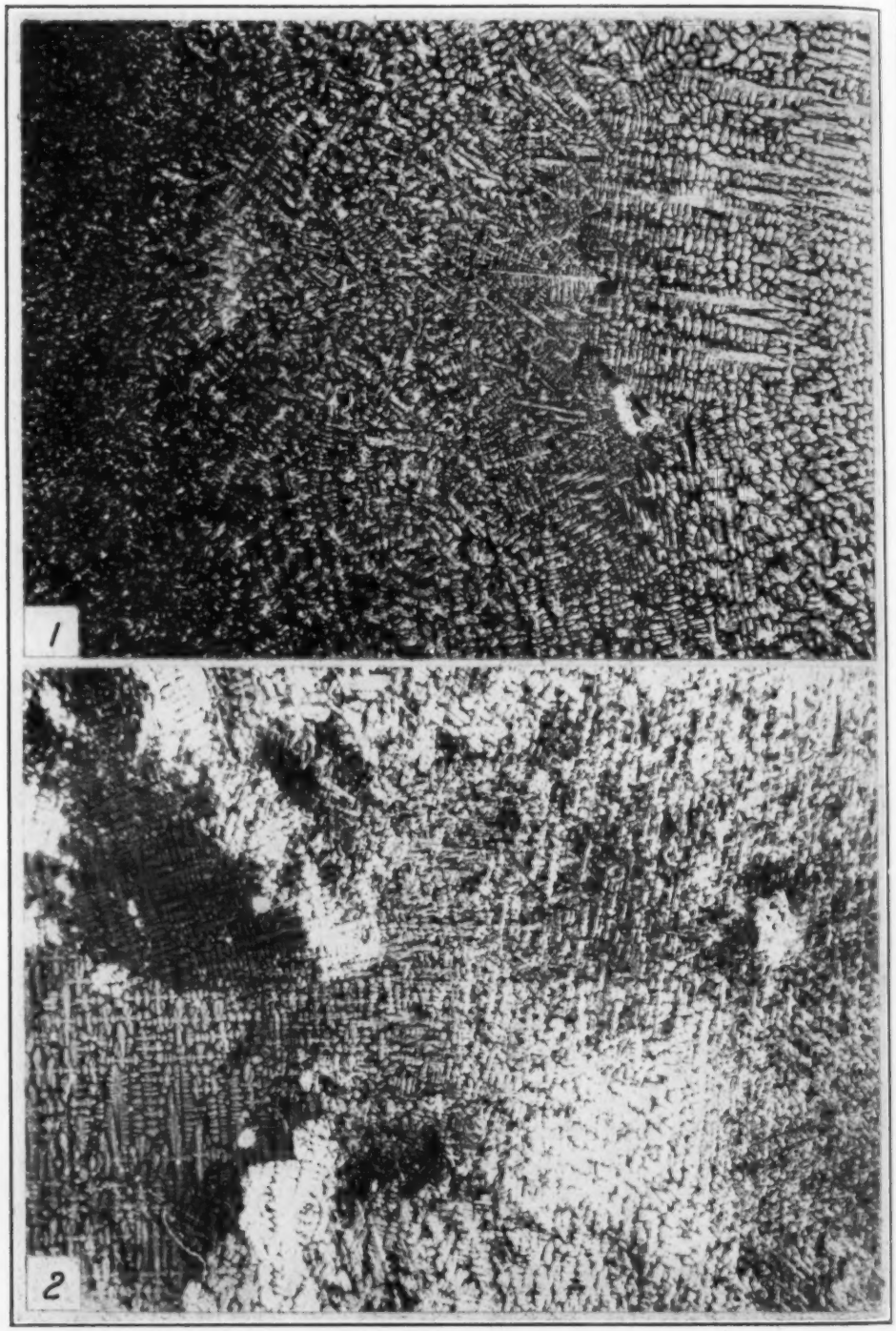


Fig. 1—Alloy Containing 0.04 Per Cent Carbon, 9.79 Per Cent Nickel in the As Cast Condition and Annealed. × 2.5
Fig. 2—Alloy Containing 0.45 Per Cent Carbon, 9.79 Per Cent Nickel, As Cast. × 2.5.

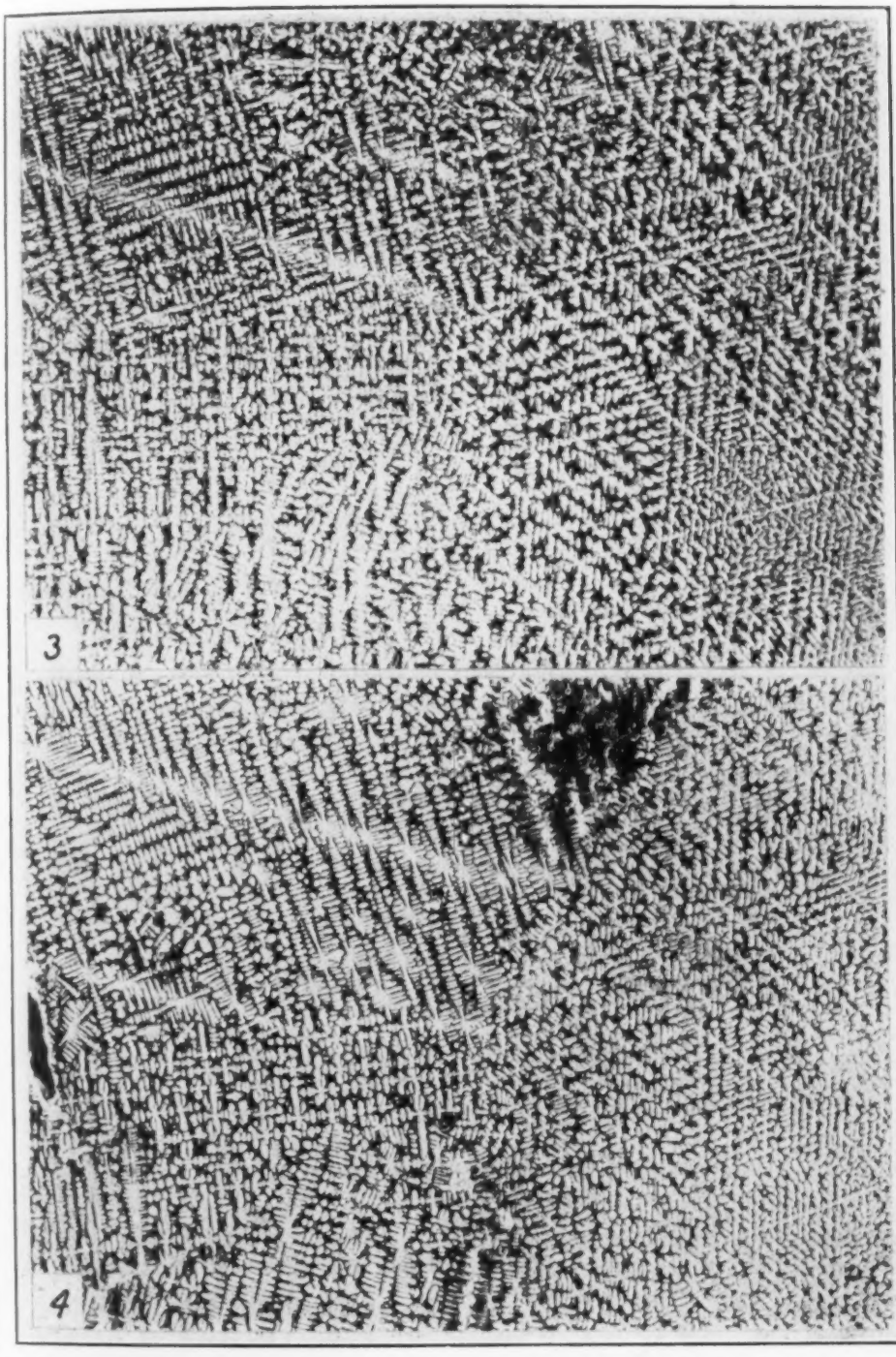


Fig. 3—Same as Fig. 2 After Drastic Annealing. × 2.5.
Fig. 4—Same Alloy as Fig. 2, As Cast and Annealed and Quenched in Ice Brine from 1000 Degrees Cent. (1830 Degrees Fahr.). × 2.5.

Fig. 5—Photomicrograph of Alloy Shown in Fig. 4. × 1000. This Photomicrograph Shows Portions of Pearlitic Axes and Martensitic Fillings.

An alloy which happened to have exactly the same amount of nickel, namely 9.79 per cent but which contained 0.45 per cent carbon exhibited in the cast condition the dendritic patterns shown in Fig. 2 and after drastic annealing the macrostructure of Fig. 3. It will be noted that annealing instead of effacing or minimizing dendritic segregation has, if anything, intensified it. This action of annealing has been repeatedly observed not only in nickel steel, but in a number of other alloy steels. The same sample after slight repolishing was heated to 1000 degrees Cent. (1830 degrees Fahr.) and quenched in iced brine. Its unaltered dendritic structure is shown in Fig. 4, an impressive evidence of the persistence of dendritic segregation. Closer examination reveals the interesting fact that in the drastically annealed sample the axes of the dendrites are pearlitic, while the fillings are martensitic. This is to be ascribed to the segregation of both carbon and nickel in the fillings which thereby became air hardening, while the axes transformed into pearlite. In Fig. 5 is shown under a magnification of 1000 diameters part of an axis and adjoining part of fillings, the former pearlitic, the latter martensitic. It follows from these considerations that on slow cooling the axes of the dendrites should transform at the usual critical temperature for nickel steel of this character (650 degrees Cent. ±) thereby becoming pearlitic, while the transformation of the fillings should be delayed

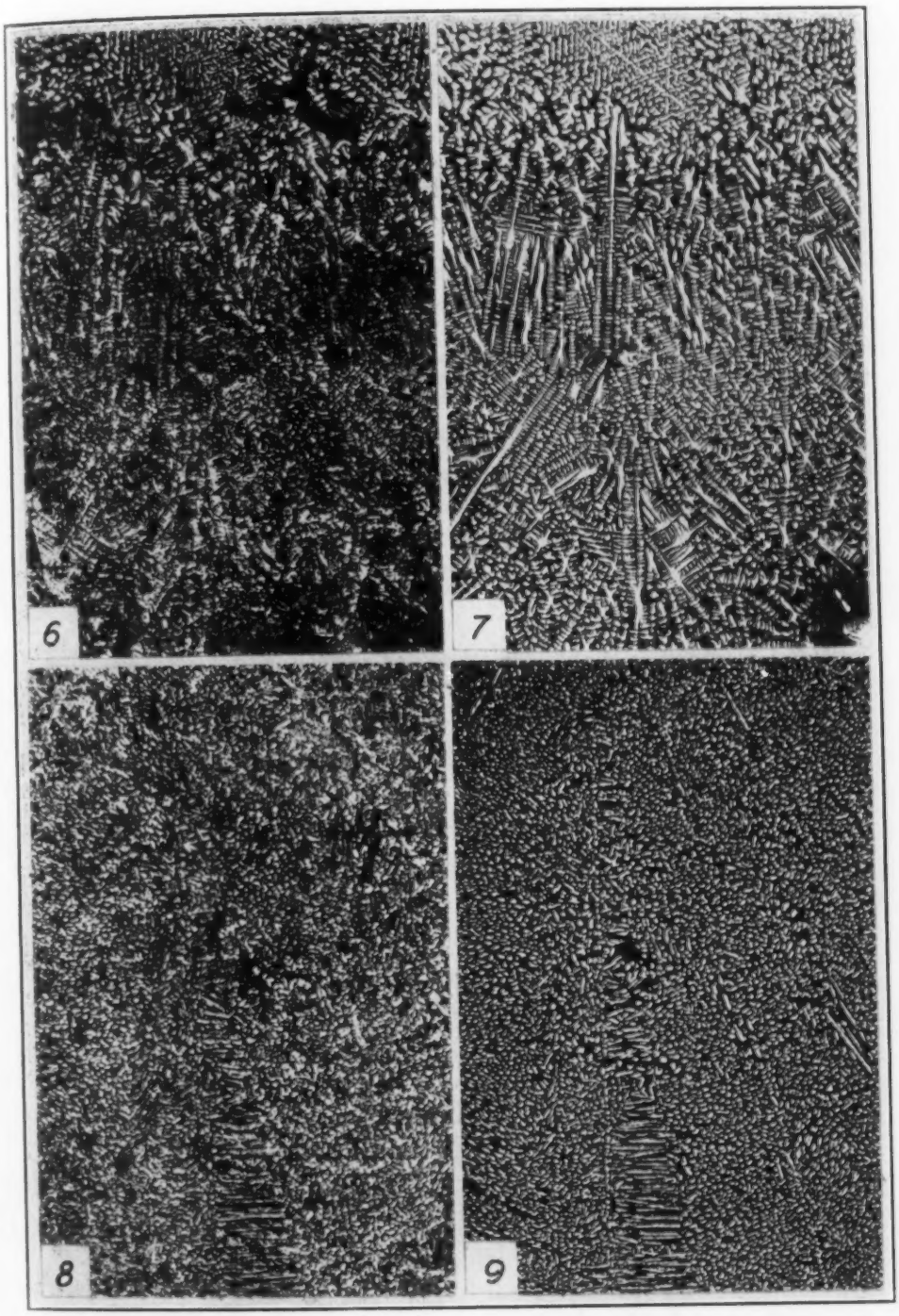


Fig. 6—Alloy Containing 0.07 Per Cent Carbon, 13.48 Per Cent Nickel, As Cast. × 2.5.
Fig. 7—Same As Fig. 6, As Cast and Annealed. × 2.5.
Fig. 8—Alloy Containing 0.05 Per Cent Carbon, 15.03 Per Cent Nickel, As Cast. × 2.5.
Fig. 9—Same as Fig. 8, As Cast and Annealed. × 2.5.

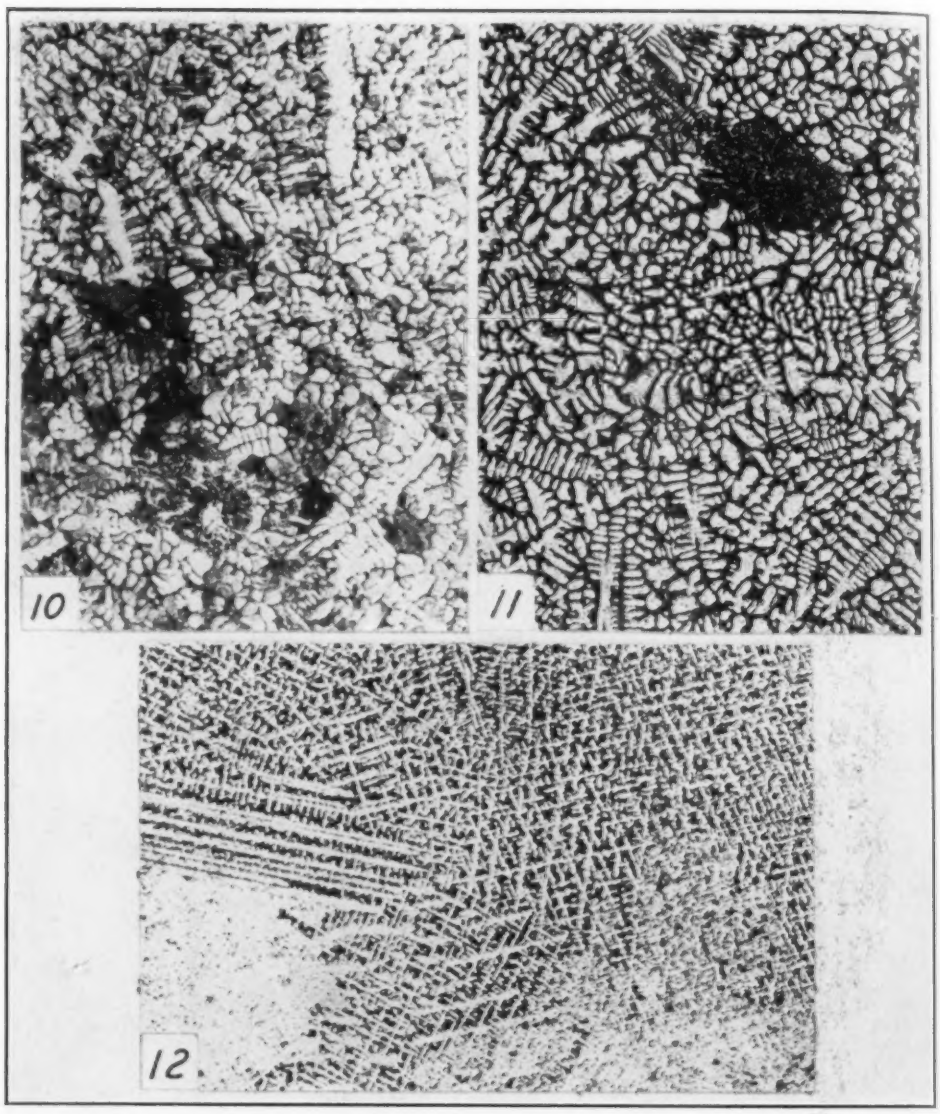


Fig. 10—Alloy Containing 0.03 Per Cent Carbon, 13.56 Per Cent Nickel, As Cast. × 2.5.
Fig. 11—Same Alloy as Fig. 10, As Cast and Annealed. × 2.5.
Fig. 12—Alloy Containing 1.06 Per Cent Carbon, 0.08 Per Cent Manganese, 0.004 Per Cent Phosphorus, 0.003 Per Cent Sulphur, and 0.017 Per Cent Silicon, As Cast. × 2.5.

until a temperature of some 300 degrees Cent. is reached when martensite is formed. Thermal-critical curves, therefore, should exhibit these two critical points and we believe that we have obtained evidence in support of this view.

An alloy containing 0.07 per cent carbon and 13.48 per cent nickel exhibited as cast the dendritic structure reproduced in Fig. 6

and, after annealing, the structure of Fig. 7. The dendrites are now more sharply outlined.

With 0.05 per cent carbon and 15.03 per cent nickel the dendrites were again sharpened by long annealing (Figs. 8 and 9). The same phenomenon is observed in Figs. 10 and 11 of an alloy containing 0.03 per cent carbon and 13.56 per cent nickel.

Many other alloys of iron, carbon and nickel were studied with similar results. It may suffice for our present purpose to offer a few conclusions which appear to be justified.

Conclusions

Nickel is capable of producing intense and persistent dendritic segregation. The addition of carbon probably increases that tendency. Drastic annealing not only fails to efface the dendritic structure but actually intensifies it. Quenching from 1000 degrees Cent. in iced brine leaves the dendritic segregation unchanged. In steels which become pearlitic after drastic annealing the axes of the dendrites consist of pearlite, while the fillings are martensitic. In steels which remain martensitic even after long annealing, it is difficult and sometimes impossible to bring out a dendritic pattern, at least with the reagents used.

Appendix

It is generally held, we believe, that in straight carbon steel, phosphorus is chiefly responsible for dendritic segregation. That this action of phosphorus is indeed very marked cannot be denied. Pronounced dendritic segregation, however, may exist when the amount of phosphorus present is negligible as can be seen from Fig. 12 showing the macrostructure of an iron-carbon alloy containing 1.06 per cent carbon, 0.08 per cent manganese, 0.004 per cent phosphorus, 0.003 per cent sulphur, and 0.17 per cent silicon. The dendritic pattern must here be ascribed chiefly to the segregation of carbon in the fillings.

DISCUSSION

Written Discussion: By H. S. Rawdon, U. S. Bureau of Standards. This interesting note with its excellent photomicrographs serves admirably to emphasize what has been known in a general way for some time concerning the pronounced tendency toward the formation of dendrites in nickel steels, and their persistence after annealing and working. This marked tendency is also observed in other nickel alloys. Even after such an alloy has been reheated and severely mechanically worked by forging so that an entirely new crystal

structure has resulted, marked evidence of the pre-existing dendritic condition often still persists. This is illustrated in the accompanying photomicrograph, which shows the structure of hot-worked monel metal. It is noteworthy that the crystal structure resulting upon heating and mechanically working is apparently independent of the dendritic condition. The grain boundaries of the crystals of the annealed structure cut across the "work lines" which are the remnants of the pre-existing dendrites.

The question may well be asked whether this marked pre-existence of the dendritic condition has any practical significance. Is forged nickel steel, for example, better or worse because of it? If one were to venture an opinion it would be that the impact resistance of notched longitudinal specimens might well be expected to be improved as a result of this condition, whereas the result would tend to be of the opposite nature when properties of the material were measured transversely.

Microstructure of Hot Forged Monel Metal Etched with Concentrated Nitric Acid. × 100.

V. N. KRIVOBOK: In regard to Dr. Sauveur's paper, may I say this—since the speaker is very much interested in dendrites, permit me to say that our knowledge of the dendritic structure is very superficial. The remarks of Mr. Rawdon were quite to the point. We do not know yet whether dendrites are detrimental or not, and wish that somebody would take up that work again.

Reply by Albert Sauveur

As Mr. Rawdon rightly remarks, it has been known in a general way for some time that nickel steel shows a tendency to pronounced dendritic segregation. It was not so well known, however, that this segregation is so persistent that drastic annealing fails to efface it. Indeed, it actually intensifies it.

I do not agree with Dr. Krivobok's opinion that our knowledge of the dendritic structure is very superficial. I wish we knew as much about many characteristics of steel as we do about its dendritic structure. That many have but a superficial knowledge of the subject, however, is undoubtedly true. I also differ with Dr. Krivobok when he states that it is not known whether dendrites are detrimental or not. A dendritic pattern implies dendritic segregation which, in turn, on forging, results in bands and directional properties, features which certainly must be considered detrimental. Of course, it does not follow that of two steels the one exhibiting the more marked dendritic structure is necessarily of relatively inferior quality. Many other factors affect the quality of the metal. If dendritic segregation, banding and directional properties could be eliminated the valuable properties of steel would be enhanced.

ENDURANCE PROPERTIES OF SOME WELL-KNOWN STEELS IN STEAM

By T. S. Fuller

Abstract

The endurance properties of nickel steel, a non-corrodible chrome-iron alloy, several nitriding steels, and an austenitic steel of the 18 per cent chromium-8 per cent nickel type have been determined in air and in steam under various conditions of temperature and pressure.

In the absence of appreciable quantities of liquid water and oxygen the endurance properties of high strength nickel steel and non-corrodible chrome-iron alloy are not adversely affected by steam atmospheres up to and including pressures of 220 pounds and temperatures of 371 degrees Cent. (700 degrees Fahr.).

In the presence of liquid water and oxygen the endurance values are not a function of the initial tensile properties of the material.

The ratio of the air-room temperature endurance limit to ultimate strength is higher in the case of the nitrided nitriding steels than in that of any of the others tested.

THE initial experiments of this investigation to determine the combined effects of steam and temperature on the endurance properties of certain steels have been described elsewhere by the present author.[1] The testing machines were designed by C. E. Weaver,[2] and are a modification of the White-Souther and McAdam types. Each is driven directly by an individual one-half horse power, 115-volt direct-current motor, running at a speed of 2200 revolutions per minute. The temperature was measured by a mercury thermometer, and the pressure by a steam gage. Endurance limits have been determined in some instances on the basis of 10×10^6, and in others on the basis of 50×10^6 cycles.

[1] T. S. Fuller, *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, pp. 280-292.

[2] Manager's Office, General Electric Co., Schenectady, N. Y.

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, T. S. Fuller, is a member of the society and is associated with the research laboratories of the General Electric Co., Schenectady, N. Y. Manuscript received May 16, 1931.

Materials Tested

Essentially of a fundamental nature, it was found necessary, in order to make the investigation comprehensive, to test materials treated to give a wide range of properties. The work reported deals with tests made on nickel steel, a non-corrodible chrome-iron alloy, two nitriding steels, and one of the 18 chromium–8 nickel type.

The materials were received in the form of bars one inch in diameter and about twelve feet long. Two tensile specimens were taken, one from one end and one from the center of each bar, the remainder being cut into 9 3/16 inch lengths for endurance specimens. All specimens were stamped with a letter indicating the material, with a number indicating the bar, and with another letter indicating the position of the specimen in the bar. After heat treatment the specimens were carefully machined, special precautions being taken to remove the metal from the reduced section a little at a time in light cuts to avoid disturbing the structure underneath the surface. The final finishing on the reduced section was done with a Norton grinder, which was provided with two formed wheels to produce the exact contour of the specimen. The wheel performing the rough finishing operation was known as No. 60K Crystollon, and the one employed for the final finish was 400-grain Grade 2 Crystollon shellac wheel, both being furnished by the Norton Co. A lubricant, also made by the same company, known as "economy grinding lubricant" was used.

A comparison of results obtained with nickel steel specimens finished by this method of grinding with those of specimens of the same material prepared with 00 emery showed a variation of less than 3 per cent, which is less than the experimental error.

Nickel Steel

Two series of tests were made on nickel steel of the 3.5 per cent nickel 0.35 per cent carbon type, one treated to have low physical properties and hereinafter designated nickel steel A, and the other treated to have higher properties, hereinafter designated nickel steel B. The properties are given in Table I.

Non-Corrodible Chrome-Iron Alloy

Three series of tests were made on a non-corrodible chrome-iron

Table I

Physical Properties of Steels Tested

Material	Ult. Str. Lbs. per Sq. In.	Yield point Lbs. per Sq. In.	Prop. Limit Lbs. per Sq. In.	Elong. in 2" per cent	Red. of area per cent	Brinell hardness	Charpy Values (Keyhole Notch) Ft. Lb.
Nickel Steel A	105,000	.....	63,000	25	59	228	21–22
Nickel Steel B	119,000	.....	97,000	25	67	255	34–36
Non-corrodible Chrome-Iron Alloy C	71,000	.....	33,000	37	74	201	..
Non-corrodible Chrome-Iron Alloy D	102,000	.....	63,000	26	70	219	..
Non-corrodible Chrome-Iron Alloy E	116,000	.....	80,000	21	66	236	..
Nitriding Steel F Before nitriding	123,000	99,000	84,000	21	62	...	45
Nitriding Steel F After nitriding	125,000	100,000	.....	13	34	...	23
Nitriding Steel G-1 Not nitrided	126,000	.....	68,000	20	60	262	40
Nitriding Steel G-2 Not nitrided	129,000	.....	83,000	19	61	263	40
Nitriding Steel H Not nitrided	127,000	.....	62,000	22	52	...	15

alloy containing 12.5 per cent chromium and 0.10 per cent carbon, heat treated to have a range of properties, the low property material being designated by the letter C, the intermediate by D, and the high property by E. The physical properties are to be found in Table I.

Nitriding Steels

Specimens of three nitriding steels were heat treated before machining. Steel F (typical composition C — 0.36, Mn — 0.51, Si — 0.27, Al — 1.23, Cr — 1.49, Mo — 0.18, S — 0.10, P — 0.013) was quenched in oil from 930 degrees Cent. (1705 degrees Fahr.) and tempered at 650 degrees Cent. (1208 degrees Fahr.); G-1 (C — 0.18, otherwise composition similar to F) was oil-quenched from 950 degrees Cent. (1740 degrees Fahr.) and tempered at 650 degrees Cent. (1200 degrees Fahr.), and G-2 (composition similar to G-1) was quenched in oil from 960 degrees Cent. (1760 degrees Fahr.) and tempered at 625 degrees Cent. (1155 degrees Fahr.). H is a nitriding steel supplied by another manufacturer. The physical properties after such heat treatments are to be found in Table I.

After machining the specimens were nitrided by heating twenty-four hours at 500 degrees Cent. (930 degrees Fahr.) in ammonia gas. The physical properties of F after this treatment are given in Table I.

Austenitic Steel

Three series of specimens of 18 per cent chromium–8 per cent nickel alloy were included, each series having a different carbon content, and being divided into nine groups, each group having had a different thermal treatment. The different series are represented by the letters I, J, and L and the thermal treatments by the numerals 1—9.

A partial analysis of the three series follows:

Series	Carbon Per Cent	Chromium Per Cent	Nickel Per Cent
I	0.065	18.77	8.91
J	0.085	18.47	9.15
L	0.15	18.24	8.08

The thermal treatment of the bars follows:

(1) Hot-rolled condition.
(2) Held six hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.
(3) Held 500 hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.
(4) Held one hour at 1066 degrees Cent. (1950 degrees Fahr.), air-cooled.
(5) Held one hour at 1066 degrees Cent. (1950 degrees Fahr.), air-cooled and six hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.
(6) Held one hour at 1066 degrees Cent. (1950 degrees Fahr.), air-cooled and 500 hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.
(7) Held one hour at 1150 degrees Cent. (2100 degrees Fahr.), water-quenched.
(8) Held one hour at 1150 degrees Cent. (2100 degrees Fahr.), water-quenched and six hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.
(9) Held one hour at 1150 degrees Cent. (2100 degrees Fahr.), water-quenched and 500 hours at 650 degrees Cent. (1200 degrees Fahr.), air-cooled.

Specimens

The type of specimen shown in a previous report[1] is arranged as a rotating cantilever beam, the reduced section of which is similar to McAdam's[3] type C specimen described in 1921. The maximum stress is in the plane whose diameter is 0.4687 inch, although the stress from the bottom of the fillet over a distance of one and one-half inches therefrom varies only 1½ per cent. The end of the specimen that fits into the chuck is ground to conform to a standard No. 3 Morse taper.

[3]D. J. McAdam, Jr., "Endurance of Steel under Repeated Stresses," *Chemical and Metallurgical Engineering*, Vol. 25, 1921, p. 1081.

Method of Test

The method followed has been to load the first specimen of a series to be tested under a given set of conditions with a stress calculated to cause failure in a comparatively short time. The load of successive specimens was then decreased in decrements of 5000 pounds per square inch until a stress was found at which the specimens withstood 10×10^6 or 50×10^6 cycles without fracture. Endurance limits were determined from this data. Temperature and pressure readings were recorded at one-half hour intervals.

Scope of Tests

Endurance limits have been determined with the specimens in air at room temperature, in air with a jet of wet steam directed at the highly stressed section, at a temperature of 77 degrees Cent. (170 degrees Fahr.) in an atmosphere of steam and air, and in steam at the indicated temperatures and pressures:

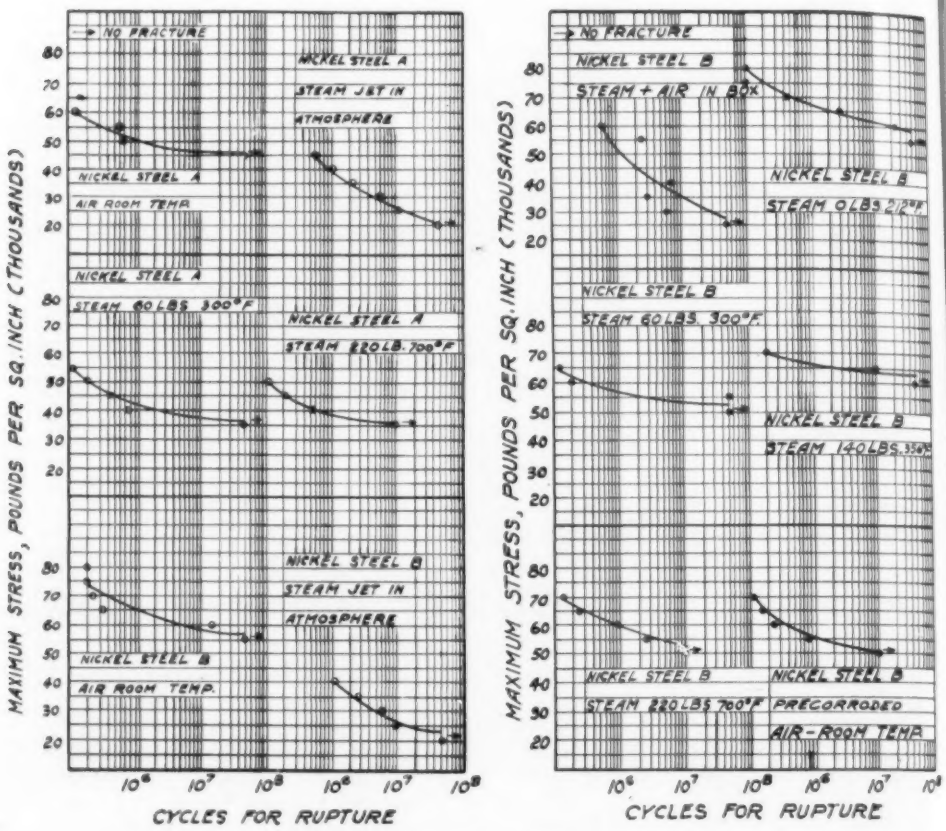
Temperature	Pressure in Pounds
100 degrees Cent. (212 degrees Fahr.)	0
149 degrees Cent. (300 degrees Fahr.)	60
180 degrees Cent. (355 degrees Fahr.)	140
371 degrees Cent. (700 degrees Fahr.)	220

The oxygen content of the steam was determined, 1 kilogram showing 0.208 grams of oxygen, which is equivalent to 0.0208 per cent by weight.

The air-room temperature and the air-steam jet tests were made in a machine to which no steam box was attached. The latter condition was particularly severe because of the presence of both liquid water and excess oxygen, the two substances necessary to cause ordinary ferrous corrosion. All other tests in steam were carried on in machines equipped with steam-tight boxes surrounding the specimens and the corrosion was not severe. The effect of the corrosion taking place in the 77 degrees Cent. (170 degrees Fahr.) steam-air experiment was of about the same magnitude as that in the air-steam jet tests.

Test Data and Results

A summary of the physical properties of the materials tested is to be found in Table I, of the endurance properties in Table II, and

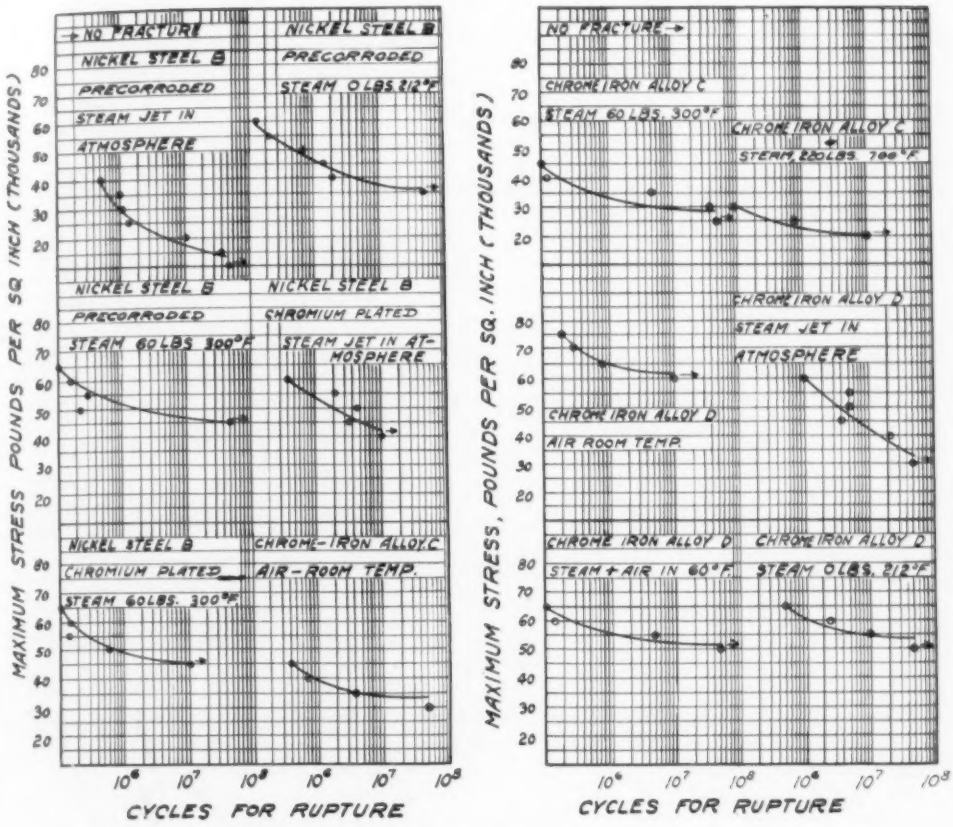


Figs. 1 and 2—Endurance Limits for Steel A and B.

the data from which the endurance limits were determined have been plotted in Figs. 1 to 13.

Nickel Steel A

The endurance limit of nickel steel A was found to be 46,000 pounds per square inch in the atmosphere at room temperature, 23,000 pounds per square inch when exposed to a jet of steam in the atmosphere, 36,000 pounds per square inch in 60 pounds steam at 149 degrees Cent. (300 degrees Fahr.) and 35,000 pounds per square inch in 220 pounds steam at 371 degrees Cent. (700 degrees Fahr.). The damaging effect due to the corrosion caused by the presence of both liquid water and oxygen at a somewhat elevated temperature is well illustrated by the drop in endurance limit in the steam jet experiment to 50 per cent of its air-room temperature value.



Figs. 3 and 4—Endurance Limits for Steel B and Chrome-Iron Alloy C and D.

Nickel Steel B

The endurance limit of this material in the air-steam jet test was found to be 24,000 pounds per square inch and may be compared with 58,000 pounds per square inch, the value found in the air-room temperature conditions, and 26,000 pounds per square inch in the steam plus air experiment in the steam box. A very casual examination discloses the tendency of the endurance properties of this steel to hold up at least to a temperature of 371 degrees Cent. (700 degrees Fahr.). It is further interesting to compare the values of 23,000 and 24,000 pounds per square inch obtained with steels A and B in the steam jet in atmosphere experiment, indicating that in cases where the corrosion is severe, the initial tensile properties of the material are not of great importance.

The pre-corroded specimens were heated in the absence of stress for one week in an atmosphere of wet steam and air and then tested

Table II

Material	Condition of Test	Endurance Limit Lbs. per Sq. In.
Nickel Steel A	Air, room temperature	46,000
	Steam jet in atmosphere	23,000
	Steam, 60 lb. 149°C. (300°F.)	36,000
	Steam, 220 lb. 371°C. (700°F.)	35,000
Nickel Steel B	Air, room temperature	58,000
	Steam jet in atmosphere	24,000
	Steam + air in box 0 lb. 76°C. (170°F.)	26,000
	Steam, 0 lb. 100°C. (212°F.)	58,000
	Steam, 60 lb. 149°C. (300°F.)	54,000
	Steam, 140 lb. 186°C. (356°F.)	64,000
	Steam, 220 lb. 371°C. (700°F.)	53,000
Nickel Steel B Pre-corroded one week.	Air, room temperature	50,000
	Steam jet in atmosphere	14,000
	Steam, 0 lb. 100°C. (212°F.)	36,000
	Steam, 60 lb. 149°C. (300°F.)	45,000
Nickel Steel B Chromium plated	Steam jet in atmosphere	42,000
	Steam, 60 lb. 149°C. (300°F.)	46,000
Non-corrodible Chrome-Iron Alloy C	Air, room temperature	34,000
	Steam, 60 lb. 149°C. (300°F.)	29,000
	Steam, 220 lb. 371°C. (700°F.)	20,000
Non-corrodible Chrome-Iron Alloy D	Air, room temperature	61,000
	Steam jet in atmosphere	33,000
	Steam + air in box 0 lb. 76°C. (170°F.)	52,000
	Steam, 0 lb. 100°C. (212°F.)	54,000
	Steam, 60 lb. 149°C. (300°F.)	55,000
	Steam, 140 lb. 186°C. (356°F.)	54,000
	Steam, 220 lb. 371°C. (700°F.)	54,000
Non-corrodible Chrome-Iron Alloy D Pre-corroded one week.	Air, room temperature	61,000
	Steam jet in atmosphere	34,000
	Steam, 0 lb. 100°C. (212°F.)	54,000
	Steam, 60 lb. 149°C. (300°F.)	54,000
Non-corrodible Chrome-Iron Alloy E	Air, room temperature	56,000
	Steam, 60 lb. 149°C. (300°F.)	54,000
Nitriding Steel F Before Nitruding	Air, room temperature	74,000
	Steam, 60 lb. 149°C. (300°F.)	64,000
	Steam, 220 lb. 371°C. (700°F.)	50,000
Nitriding Steel F Nitrided	Air, room temperature	91,000
	Steam jet in atmosphere	73,000
	Steam, 60 lb. 149°C. (300°F.)	69,000
	Steam, 220 lb. 371°C. (700°F.)	58,000
Nitriding Steel G-1 Nitrided	Air, room temperature	65,000
	Steam jet in atmosphere	62,000
	Steam, 60 lb. 149°C. (300°F.)	69,000
	Steam, 220 lb. 371°C. (700°F.)	54,000
Nitriding Steel G-2 Nitrided	Air, room temperature	74,000
	Steam jet in atmosphere	71,000
	Steam, 60 lb. 149°C. (300°F.)	69,000
	Steam, 220 lb. 371°C. (700°F.)	53,000
Nitriding Steel H Nitrided	Air, room temperature	92,000
Nitriding Steel F Nitrided 500°C. (932°F.)	Steam, 60 lb. 149°C. (300°F.)	72,000
Nitriding Steel F Nitrided 500°C. (932°F.) Notched	Steam, 60 lb. 149°C. (300°F.)	60,000

Table II—Continued

Condition of Test—Steam, 60 lb. 149°C. (300°F.)					
Material 18 chromium—8 nickel steel	Endurance Limit Lbs. per Sq. In.	Material 18 chromium—8 nickel steel	Endurance Limit Lbs. per Sq. In.	Material 18 chromium—8 nickel steel	Endurance Limit Lbs. per Sq. In.
I—1	46,000	J—1	51,000	L—1	56,000
I—2	45,000	J—2	51,000	L—2	46,000
I—3	34,000	J—3	21,000	L—3	40,000
I—4	22,500	J—4	26,000	L—4	26,000
I—5	25,000	J—5	22,500	L—5	28,000
I—6	25,000	J—6	21,000	L—6	21,000
I—7	24,000	J—7	21,000	L—7	34,000
I—8	21,000	J—8	21,000	L—8	23,000
I—9	21,000	J—9	21,000	L—9	21,000

under the conditions indicated in Table II. The pre-corroded B specimens showed an air-room temperature value of 50,000 pounds per square inch which, when compared with the B steam jet in atmosphere value of 24,000 pounds per square inch, further emphasizes the fact pointed out so many times by D. J. McAdam, Jr. that corrosion without stress is very much less damaging than corrosion with stress. Furthermore the pre-corroded B value of 14,000 pounds per square inch in the steam jet atmosphere experiment is the lowest obtained in the tests under consideration.

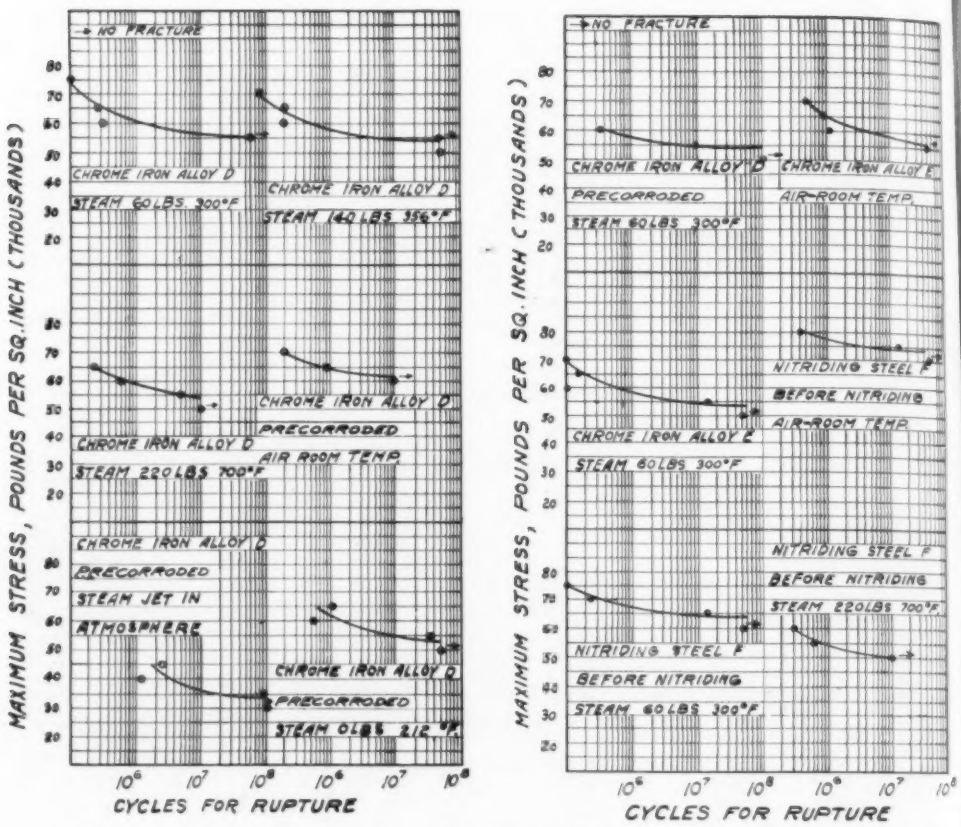
The value of 42,000 pounds per square inch, shown by the chromium plated B specimens in the steam jet-atmosphere test, indicates a rather effective protection offered by the plating during the period of the test. How effective such protection might be over a long period of time may be open to question.

Non-Corrodible Chrome-Iron Alloy C

The low property chrome-iron alloy designated C showed an appreciable falling off in endurance limit with increasing temperature.

Non-Corrodible Chrome-Iron Alloy D

The endurance properties of the high property chrome-iron alloy designated D, like those of the high property nickel steel, showed a pronounced tendency to hold up at least to a temperature of 371 degrees Cent. (700 degrees Fahr.). The steam jet in atmosphere endurance value of steel D was 54 per cent of its air-room temperature value against a corresponding value of 41 per cent for nickel steel B. This result is not surprising in view of the relative corrosion resist-



Figs. 5 and 6—Endurance Limits for Chrome-Iron and Steel F Nitriding Steel.

ance of the two steels. The spread between the steam jet in atmosphere and steam plus air in box values of D is much greater than the case of nickel steel B, being 57 per cent in the former instance and 8 per cent in the latter. This again can be explained by the relative corrosion resistance of the two steels under consideration.

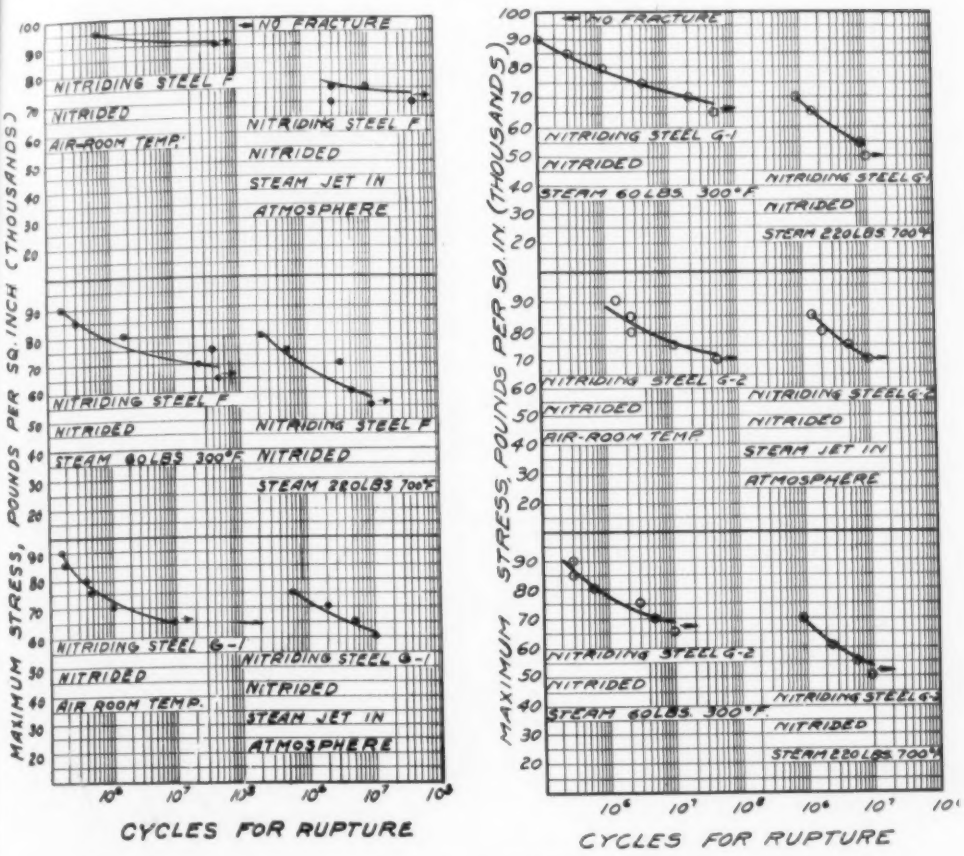
The results obtained with the specimens of steel D which were pre-corroded one week in an atmosphere of wet steam and air showed no damage due to this type of stressless corrosion.

Non-Corrodible Chrome-Iron Alloy E

Tests indicated the endurance properties of steel E to be similar to those of D.

Nitriding Steel F

Considered as a group the endurance properties of the nitrided nitriding steels are surprising. Steel F, before nitriding, showed

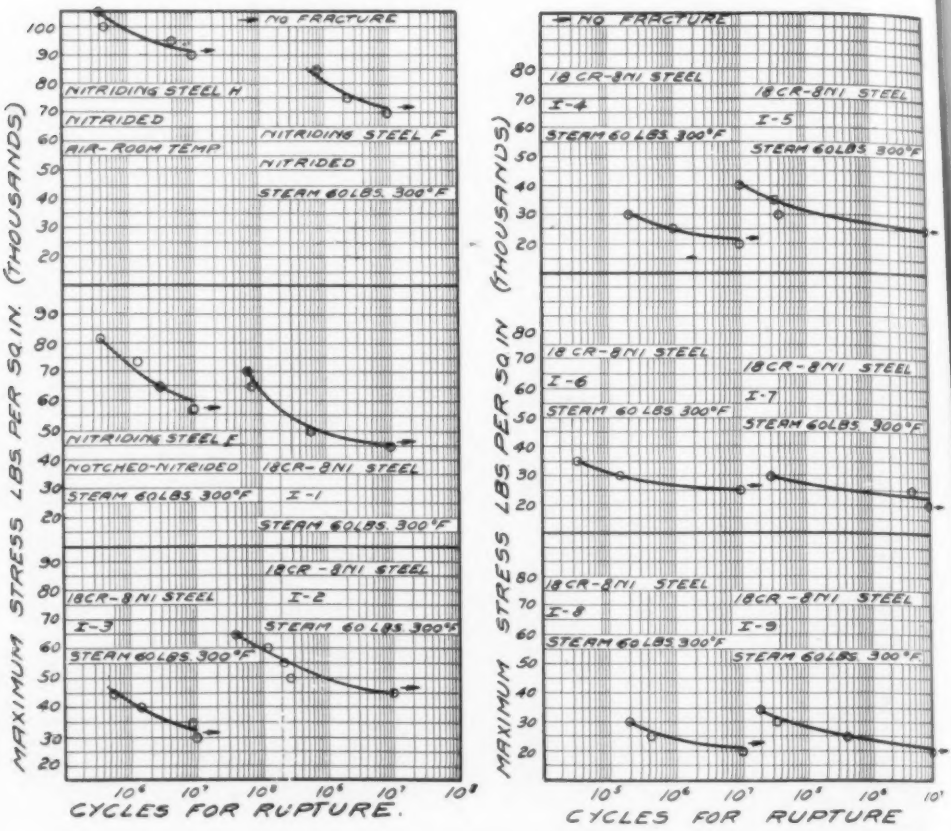


Figs. 7 and 8—Endurance Limits for Nitriding Steel F, Steel G-1 and G-2.

values ranging from 74,000 pounds per square inch in air at room temperature to 50,000 pounds per square inch in 220 pounds steam at 371 degrees Cent. (700 degrees Fahr.). Nitrided specimens showed an air-room temperature value of 91,000 pounds per square inch and a steam jet in atmosphere value of 73,000 pounds per square inch which is outstanding when compared with the corresponding values of steels B and D. The tendency is for the endurance properties of the nitrided nitriding steels to hold up rather less well with increasing temperature than steels B and D, although the value of 58,000 pounds per square inch obtained with steel F is the highest shown in the 220-pound steam at 371 degrees Cent. (700 degrees Fahr.) tests.

Nitriding Steels G-1 and G-2

The endurance properties shown by steels G-1 and G-2 were those to be expected of lower carbon material.



Figs. 9 and 10—Endurance Limits for Nitriding Steel F and for 18 and 8 Corrosion Resisting Steels.

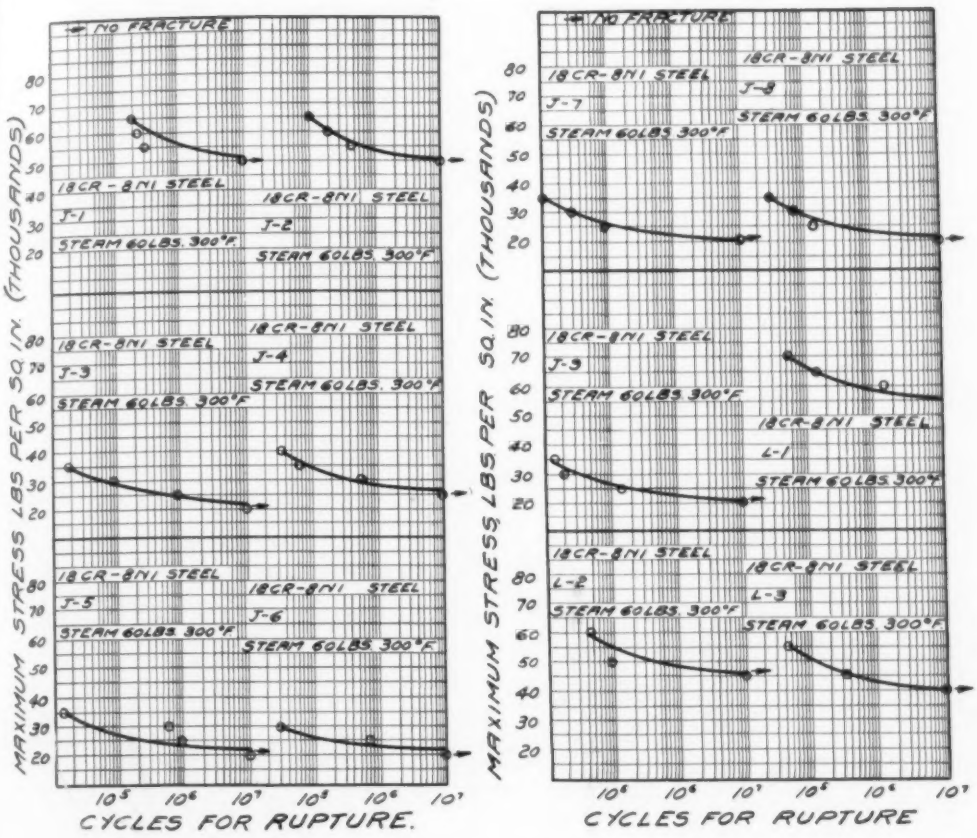
Nitriding Steel H

The air-room temperature properties of nitrided H specimens were similar to those of steel F.

Effect of a Notch on the Endurance Properties of Nitrided Specimens

To determine the effect of a notch, specimens were machined as usual, whereupon a 45-degree notch 0.035 inch in depth, having a 0.010-inch radius at the bottom, was cut in each at the plane of maximum stress, after which the specimens were nitrided. In calculating the stress of notched specimens the value of the diameter at the base of the notch was used, but no factor for the stress concentration at this point was added.

In 60-pound steam at 149 degrees Cent. (300 degrees Fahr.) standard specimens of steel F, which had been nitrided by heating



Figs. 11 and 12—Endurance Limits for 18 and 8 Corrosion Resisting Steels.

twenty-four hours in ammonia at 500 degrees Cent. (930 degrees Fahr.), showed an endurance limit of 72,000 pounds per square inch and notched specimens 60,000 pounds per square inch.

18 Chromium–8 Nickel Steel

The effect of prolonged heating at elevated temperatures on the endurance properties in 60-pound steam at 149 degrees Cent. (300 degrees Fahr.) of this well-known alloy has been determined. In the hot-rolled condition the endurance values bear a relationship to carbon content. This relation, however, disappears after drastic treatment at elevated temperatures.

Conclusions

The facts set forth in this paper are in accord with the following conclusions:

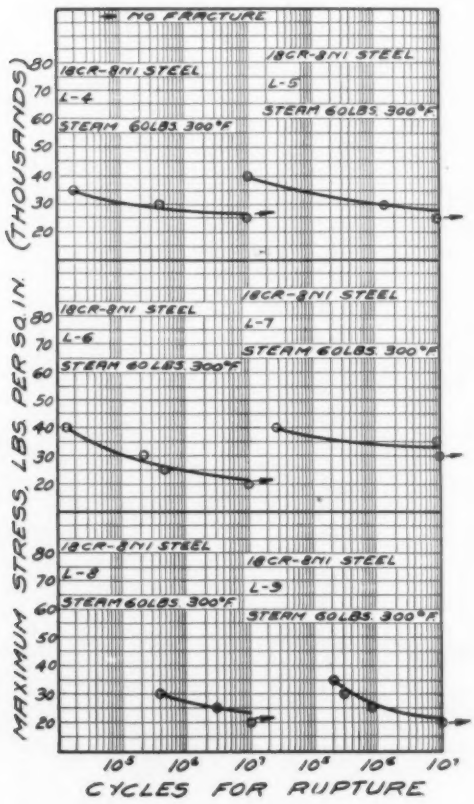


Fig. 13—Endurance Limits for 18 and 8 Corrosion Resisting Steels.

(1) The endurance properties of nickel steel B, and non-corrodible chrome-iron alloy D, in the absence of appreciable quantities of liquid water and oxygen were not adversely affected by steam atmospheres up to and including pressures of 220 pounds and temperatures of 371 degrees Cent. (700 degrees Fahr.).

(2) Due to the presence of liquid water and oxygen, the steam jet-atmosphere endurance values of steels B and D were but 41 and 54 per cent of the corresponding air-room temperature values.

(3) As evidenced by the steam jet-atmosphere tests of steels A and B, if the corrosion be severe, the endurance values are not a function of the initial tensile properties of the material.

(4) A comparison of the steam jet in atmosphere and pre-corroded air-room temperature values of steel B further empha-

sizes the damaging effect of the simultaneous presence of stress and corrosion.

(5) A chromium plate offered considerable protection to steel B against the corrosion of the steam jet-atmosphere test.

(6) No damaging effect of the pre-corrosion treatment on steel D was evidenced by any of the four tests carried out thereon.

(7) The ratio of the air-room temperature endurance limit to ultimate strength was higher in the case of the nitrided nitriding steels than in that of any of the others tested.

(8) A marked tendency of the endurance values of the nitrided nitriding steels to drop off with increasing temperature was observed.

(9) The ratio of the steam jet-atmosphere to air-room temperature endurance values was higher in the case of the nitrided nitriding steels than in that of the other steels tested.

(10) The 60-pound steam at 149 degrees Cent. (300 degrees Fahr.) endurance value of notched nitrided specimens ranged from 74 to 83 per cent of that shown by corresponding unnotched specimens.

(11) The endurance properties of the 18 per cent chromium–8 per cent nickel type of alloy are seriously affected by long intervals of time at temperatures of 650 degrees Cent. (1200 degrees Fahr.) and above.

(12) In the hot-rolled condition the endurance values of this alloy bear a relationship to carbon content. This relation, however, disappears after drastic treatment at elevated temperatures.

ACKNOWLEDGMENT

The author takes this opportunity to express his appreciation of the excellent work of Martin D. Collins who was charged with the responsibility of making the tests described in this paper.

DISCUSSION

Written Discussion: By T. McLean Jasper, A. O. Smith Corporation, Milwaukee.

I am much interested in this paper from the standpoint of the application of fatigue to service conditions in the steam industry.

In Table II are given the values of the endurance limit under various temperatures and steam pressures. It is interesting to note that steam mixed with air, which does not represent a service fatigue condition, produces a much

lower endurance limit than is the case when the specimen is confined in steam under the operating condition of pressure and temperature, and in the normal absence of free air.

In bulletin 152 of the engineering experiment station of the University of Illinois, dated November, 1925, are presented some curves on the endurance limits of various steels at various temperatures. In general it was found that the endurance limit decreases as the temperature of test is increased even in dry air. It is also known that the long time strength of steel decreases in general with increasing temperature.

The author has produced a fine example representing a close simulation of service conditions of testing metals which are appropriate for use in steam power production. This should restore confidence to designers of equipment of this nature and give them starting values from which to assume working stresses in the steam industry where fatigue plays an important role.

Written Discussion: By F. N. Speller and I. B. McCorkle, department of research, National Tube Company, Pittsburgh.

The experiments cited in Mr. Fuller's paper again indicate the importance of using pure steam in connection with steam turbines. This can be obtained by the use of suitable water treatment and thorough deaeration.

As steam practically free from oxygen often contains a certain amount of free carbonic acid, it would be useful to determine whether the latter is injurious in steam with low oxygen content. The amount of oxygen in the steam used in these tests is rather high for a modern well-equipped steam plant.

The tests on the 18-chromium–8-nickel steels are most interesting. The prolonged heating at 650 degrees Cent. would be expected to cause profuse precipitation of carbides at the grain boundaries and hence to diminish the corrosion-resistance of the metal. Since tests on other materials showed that the steam used in this series was corrosive, it is not surprising that "corrosion fatigue" lowered considerably the endurance limit of these specimens under that of the hot-rolled stock. However, the results of tests under conditions 4 and 7 are not consistent with this conclusion. The latter is a treatment which is recommended to put the material in *good* structural condition, from the standpoint of corrosion-resistance, while treatment 4 is a close approach to it. Yet after receiving these treatments (4 and 7) the endurance limit is as low (or lower) than the treatment which is supposed to put it in the *worst* structural condition from the standpoint of corrosion. In the writers' opinion the metal after receiving either of the two treatments would be at least as corrosion-resistant as in the hot-rolled state.

If the above reasoning is sound, why did all the materials reheated to the higher temperatures show so much lowering of the endurance limit? The following is offered as an explanation, which the author can probably confirm or refute: It is probable that the finishing temperature of a 1-inch hot-rolled bar of 18-8 is so low that the metal will receive considerable work hardening, thereby raising the tensile strength and yield point. Treatments 4 and 7 should restore the values of these properties to considerably lower figures. The endurance limit of ferrous metals in air is roughly a function of the tensile strength, and it furthermore seldom (if ever) exceeds the yield point. The

tensile strength and yield point of the "hot-rolled" stock can have a very high value, while these values for the metal after treatments 4 and 7 would be expected to be in the neighborhood of 90,000 pounds per square inch and 32,000 pounds per square inch respectively. Even treatments 2 and 3 would be expected to lower these properties to a certain extent. A series of corrosion-fatigue tests on these metals "in air" after the various treatments would throw considerable light on the whole subject.

Written Discussion: By B. P. Haigh, Royal Naval College, Greenwich, S. E.10, England.

Mr. Fuller's investigation of the effects of steam and air on different steels subject to cyclic stress will be of great service not only to those engaged in practice but also in the foundation of a theory of this example of combined chemical and mechanical action.

It is important first to grasp the outstanding conclusion, that the effect of corrosion prior to a fatigue test is only slight in comparison with that of simultaneous action. This conclusion, which was first published[1] by the present writer in 1917, marks the characteristic difference between "ordinary mechanical" fatigue and the "combined chemical and mechanical action" that is now so generally known as "corrosion fatigue."

It is important also to note that Mr. Fuller's investigation completely supports the conclusion reached by Professor Jenkins in experiments carried out at Oxford in 1925. In comparative Woehler tests on a steel containing 0.33 per cent carbon, fatigue limits as follow were found under different conditions:

	Degrees Cent.	Pounds per Square Inch
In air	at 17	41,000
In distilled water	96	38,500
In sodium-chloride solution	96	41,250
In sodium-nitrate solution	96	39,000
In ammonium-nitrate solution	96	32,500

The results of these tests were held at first completely to negative the reality of the combined "chemical and mechanical" action; but it was suggested that the almost complete absence of the action at 96 degrees Cent. might be due to the absence of air in solution at this temperature; and when further tests were carried out with solutions of common salt allowed to drip on a steel containing 0.90 per cent carbon at ordinary air temperature, positive results were obtained as follows:

	Pounds per Square Inch
Dry pieces tested in air	38,000
Solution dripping through air	16,800
Solution dripping through hydrogen	20,400

The general conclusion drawn from these experiments was that air present in solution in the reagent constitutes the primary agent in the combined chemical

[1]B. P. Haigh, "Endurance of Brasses Under Alternating and Pulsating Stresses," Institute of Metals, London, 1917.

and mechanical action; and this conclusion appears to be strongly fortified by the results of Mr. Fuller's careful investigation.

The same conclusion may be drawn also from a series of experiments carried out by Jones[2] and the present writer, on lead and lead alloys as used for cable sheathing. By adopting suitable precautions to exclude air from the surfaces of pieces subjected to cyclic stress, the fatigue limits of lead and lead alloys were raised so far that brittle fracture was no longer possible under the ranges of stress that could be imposed without causing excessive plastic deformation.

In spite of this general conclusion, that air is commonly the agent that provokes combined chemical and mechanical fatigue, it should be borne in mind that drops of water moving at high speeds are liable to produce such high stresses that erosion and fatigue may occur even in the absence of air.

For this reason it would appear desirable that Mr. Fuller should add to the present paper a note indicating the approximate speed of the jets used in the tests. At higher speeds, it is possible that moist steam would have reduced the fatigue limit appreciably even in the absence of air.

Author's Closure

Mr. Jasper has emphasized the damaging action of air in the steam upon the endurance properties of the metals tested. This is very important.

Messrs. Speller and McCorkle have pointed out that hot-rolled 18-chromium–8-nickel stock which had been rapidly cooled from 1066 to 1150 degrees Cent. would be expected to show a corrosion-resistance superior to the same steel which had been exposed to prolonged heating at 650 degrees Cent., and hence higher endurance limits under steam conditions. Inasmuch as this was found not to be the case Speller and McCorkle suggest that the anticipated effect of the heat treatment has been masked by an annealing effect occurring simultaneously. This is the most logical explanation which has been advanced to explain the anomalies in the results of heat treatments 4 and 7 when compared to the others in the 18-chromium–8-nickel series.

It has been very good of Professor Haigh to point out that the results set forth in this paper are in accord with those previously reported by Jenkins, Jones and himself. Professor Haigh has also called attention to the fact that drops of water moving at high speeds are liable to produce such high stresses that erosion and fatigue may occur even in the absence of air. In none of the tests reported in the present paper has the velocity of the steam been greater than 100 feet per second.

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[2]B. P. Haigh and Brinley Jones, "Atmospheric Action in Relation to Fatigue in Lead," Institute of Metals, London, 1930.

HARDNESS OF CHROMIUM AS DETERMINED BY THE VICKERS-BRINELL, BIERBAUM, AND MOHS METHODS

By Richard Schneidewind

Abstract

The hardness of electrodeposited chromium was found to be 625 Brinell, 8 on the Mohs scale, and gave a scratch width of 2 microns with the Bierbaum microcharacter. Heating at 290 degrees Cent. caused a sudden drop in hardness due probably to the volatilization of hydrogen. After this treatment it was found to be 250 Brinell, 5.5 on the Mohs scale, and gave a scratch width of 4.15 microns with the Bierbaum apparatus. Further heating at 1050 degrees Cent. caused the hardness to drop to about 135 Brinell, 4.5 on the Mohs scale, and to give a Bierbaum scratch width of 5.5 microns.

No exact relationships could be found between hardness of metals as measured by the three methods mentioned, although the logarithms of the Brinell and Mohs hardnesses for pure annealed metals seem to be related fairly well.

THERE has been considerable discussion regarding the great hardness and resistance to wear of electrodeposited chromium. Investigators have, with a few exceptions, however, applied these terms somewhat loosely and in a qualitative way. Investigations, the results of which are presented in this paper, had for their main purpose the securing of certain quantitative measurements which it was hoped could be expressed in practical units. The study included a consideration of comparative hardness of chromium plate and of cast annealed chromium, and the expression of hardness in different units. It was necessary to check the somewhat divergent results given in the literature by various investigators and also to make measurements of the hardness of many metals by various methods in order to convert the hardness results of chromium plate into Brinell units.

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, Richard Schneidewind, is a member of the society and is research engineer, Department of Engineering Research, University of Michigan, Ann Arbor, Michigan. Manuscript received April 3, 1931.

Hardness of Chromium Plate

The hardness of electrodeposited chromium has been given by various investigators in units which permit no comparison. In some cases approximate methods of conversion indicate that the results are widely divergent.

Hardness Values as Reported in the Literature

Rydberg,[1] Landolt-Börnstein,[2] the Smithsonian tables, and various standard handbooks assign a Mohs scratch hardness of 9 to chromium which, however, was not deposited electrolytically. For comparison, diamond is 10, topaz is 8, quartz is 7, feldspar is 6, and calcite is 3. Grant and Grant[3] obtained a Bierbaum scratch width of 1.68 to 3.68 microns on electrodeposited chromium and compared this with a scratch 2.03 microns in width for nitrided steel, 2.30 microns for hardened high carbon steel, and 4.86 microns for the same steel annealed. Hughes[4] was able to scratch chromium plate with his thumb nail.

Sargent[5] used a rebound apparatus, the scleroscope, which gave a hardness of 75 to chromium plate. Ordinary conversion tables would place this equivalent to about 575 Brinell hardness.

The Brinell hardness numbers are the ones most familiar to metallurgists, hence every effort should be made to convert as accurately as possible hardness measurements of other systems to the Brinell system. MacNaughtan[6] ascribes a Brinell hardness of between 500 and 600 to dull gray chromium plate and 900 to bright chromium plate. It is unfortunate that no details of the experimental work are given since to the writer's knowledge it would be extremely difficult to make a direct measurement because of the brittleness of the metal. Edwards[7] obtained a Brinell hardness of 91 on a speci-

[1] J. R. Rydberg, *Zeitung für phys. Chemie,* Vol. 33, 1900, p. 353.

[2] Landolt-Börnstein, *Phys. Chem. Tabellen,* 5th edition.

[3] L. E. Grant and L. F. Grant, *Transactions,* American Electrochemical Society, Vol. 53, 1928, p. 514.

[4] W. E. Hughes, "Modern Electroplating," 1922, p. 138.

[5] G. J. Sargent, *Transactions,* American Electrochemical Society, Vol. 37, 1920, p. 495.

[6] D. J. MacNaughtan and A. W. Nothershall (quoted) *Brass World,* Vol. 26, 1930, p. 159.

[7] C. A. Edwards, *Journal,* Institute of Metals, Vol. 20, 1918, p. 87.

men of chromium (not electrodeposited) from the British Museum. It is likely that this value was not obtained by direct measurement but was converted from a scleroscope result. Adcock[8] checked this result, using electrodeposited chromium melted in hydrogen. A study of these results indicates fairly wide divergence. At one extreme is Hughes' chromium capable of being scratched with the thumb nail, and at the other, MacNaughtan's chromium, 900 Brinell numbers hard.

Hardness of Metals in General

The subject of hardness or the resistance to deformation by indentation or abrasion has been attacked from a theoretical angle by many investigators. It may be of interest to compare that of chromium arrived at from theory with the values obtained experimentally. Benedicks[9] ascribes hardness in general to the closeness of the packing of the atoms. Goldschmidt[10] found that for various series of alloys and crystalline salts the Mohs hardness is an inverse function of the distance representing the closest approach of the atoms.

Traube[11] found that the scratch hardness of metals measured on the Mohs scale is approximately a function of the inner pressure of the atom which he calculated from Van der Waals' equation. Richards[12] arrived at the inner pressure thermodynamically by the equation $Cdt = Pdv$. P is the inner pressure against which heat energy does work during a change in temperature. C is the molecular heat capacity, t is the temperature, and v is volume; dt is taken as 1 degree Cent. and dv the molecular volume times the coefficient of cubical expansion. This equation can be reduced so that P in megadynes per square centimeter equals the heat capacity in joules per gram times the density divided by the coefficient of cubical expansion. Unless the units are important it is more convenient to use the readily available figures of specific heat in calories per gram and the co-

[8]F. Adcock, *Journal*, Iron and Steel Institute, 1927.

[9]C. Benedicks, "Metallurgical Researches," McGraw-Hill Book Co., 1926, p. 57.

[10]V. M. Goldschmidt, Skrifter utgitt av det Norske Videnskaps-Akademie i Oslo, 1. Mat Naturvid. Klasse, 1926. No. 8.

[11]I. Traube, *Zeitung für anorg. Chemie*, Vol. 34, 1903, p. 413.

[12]T. W. Richards, *Zeitung für phys. Chemie*, Vol. 40, 1902, p. 176.

Table I

An Approximation in Correlating Hardness With Inner Stress

Material	Specific Heat, C Cal/gram	Coefficient of Linear Expansion, E x 10^{-4}	Quotient C/E	Hardness Mohs scale
	METALS			
Chromium	0.1110	0.0840	1.32	9.0
Osmium	0.3110	0.0657	4.73	7.0
Iridium	0.3230	0.0658	4.90	6.5
Ruthenium	0.0611	0.0960	6.36	6.5
Manganese	0.1211	0.2161	0.56	5.0
Palladium	0.0592	0.1186	0.50	4.8
Iron	0.1062	0.1252	0.85	4.5
Platinum	0.3020	0.0890	3.39	4.3
Arsenic	0.0830	0.0559	1.49	3.5
Copper	0.0936	0.1640	0.57	3.0
Antimony	0.0503	0.1088	0.46	3.0
Aluminum	0.2127	0.2380	0.89	2.9
Silver	0.0560	0.1925	0.29	2.7
Gold	0.0316	0.1431	0.22	2.5
Bismuth	0.0300	0.1367	0.22	2.5
Zinc	0.0944	0.2741	0.34	2.5
Tellurium	0.0483	0.3687	0.13	2.3
Cadmium	0.0549	0.2693	0.20	2.0
Magnesium	0.2475	0.2507	0.99	2.0
Tin	0.0551	0.2703	0.20	1.8
Lead	0.0310	0.293	0.11	1.5
Indium	0.0569	0.4170	0.14	1.2
	NON-METALS			
Diamond, C	0.1130	0.0132	8.56	10.0
Silicon, Si	0.1710	0.0249	6.87	7.0
Marble $CaCO_3$	0.2120	0.1170	1.80	3.5
Lead Sulphide PbS	0.0529	0.0843	0.627	2.8
Rock Salt NaCl	0.2190	0.4040	0.54	2.5
Pot. Chloride KCl	0.1661	0.3803	0.437	2.3
Pot. Bromide KBr	0.1033	0.4201	0.246	2.3
Pot. Iodide KI	0.8190	0.4265	0.193	2.2

efficient of linear expansion since these differ only by constant or approximately constant factors. There is satisfactory agreement between these values and those obtained by Traube from Van der Waal's equation.

A rough relationship was found by plotting these various values against the Mohs hardness. A much better approximation is reached by using simply the quotient of the specific heat divided by the coefficient of linear expansion. Although there seems to be less theoretical justification these figures bear a closer relationship to the hardness than the inner pressure figures of Traube or Richards or the atomic distance values of Goldschmidt. Hardness values are assumed to be those of the soft, annealed metal. Table I presents the results of this procedure on all the metals for which data could be found. All figures were chosen for temperatures as near as possible to room temperature. A few crystalline non-metals are included for which complete data could be found. Fig. 1 shows a curve in which

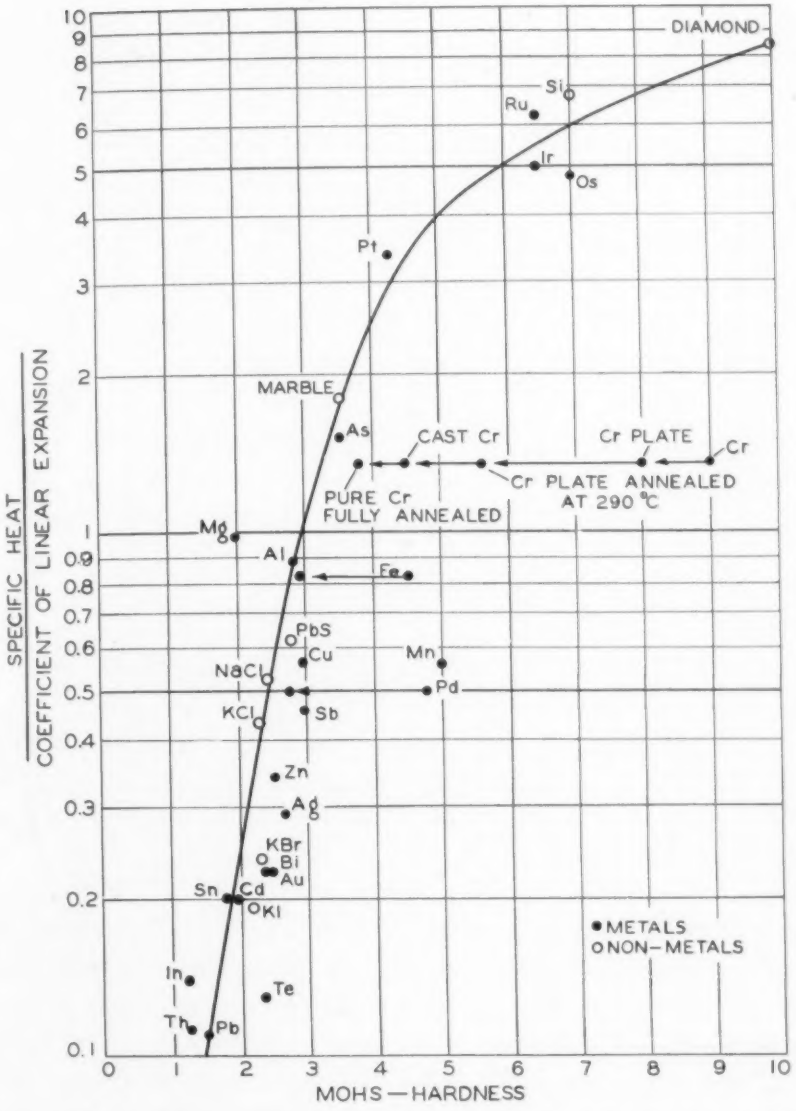

Fig. 1—Relationship Between Mohs Hardness and the Quotient of Specific Heat Divided by the Coefficient of Linear Expansion.

the Mohs hardness is plotted against the quotient expressing a measure of the approximate inner pressure of the atom.

Although the points do not fall upon this curve exactly, in most cases they come as close as Mohs hardness can be read, that is, 0.5 point, and hence it seems that this approximation shall prove valuable. Four elements stand out since they fall at a considerable distance from the curve. These are iron, palladium, manganese, and chromium. For this reason a specimen of pure sheet palladium was

annealed for 20 minutes at 1000 degrees Cent. (1830 degrees Fahr.) and cooled slowly. A test crystal of a Mohs hardness of 2 failed to scratch it while the test crystal of hardness 3 did leave a mark. Hence, an estimate would place the Mohs hardness at 2.5. This experimental value places palladium well on the curve.

Similarly, a specimen of electrolytic iron was annealed for 20 minutes at 1050 degrees Cent. (1920 degrees Fahr.) and cooled slowly. Its hardness proved to be about 2.8 since the test crystal of hardness 3 left a shallower mark than on the palladium mentioned above. This new value places iron also on the curve.

An attempt was made to recheck the hardness value of manganese but pure manganese prepared by distillation was not available at the time.

Chromium seems to behave the most abnormally; according to Traube's approximation it should be harder than most metals but much softer than the figure assigned to it.

Hardness Measurements of Chromium Plate

For the purpose of this study deposits of chromium over a millimeter in thickness were prepared by plating for 36 hours at 45 degrees Cent. (113 degrees Fahr.) and 10 amperes per square decimeter, from a bath containing initially 250 grams of chromic acid and 2.5 grams of sulphuric acid per liter of solution. The metal was deposited upon buffed brass tubes 1.5 centimeters in diameter. The smoothness and even thickness of the deposits indicated satisfactory uniformity of current density during plating. The tubes were cut into specimens about 2 centimeters in length and the base metal was dissolved away in nitric acid. This last step was not necessary for the purpose of measuring the hardness of the deposit as plated but was found expedient for the other experiments which will be described.

One such specimen was mounted in Wood's metal and was polished longitudinally for metallographic examination. Fig. 2 shows the appearance of the material in the unetched condition. A large number of voids or inclusions can be seen.

Due to the brittleness and comparative thinness of the electrodeposit, about 1 millimeter, Brinell hardness measurements were impossible on the chromium specimens. A Rockwell impression with a diamond point was attempted but the material cracked and no read-

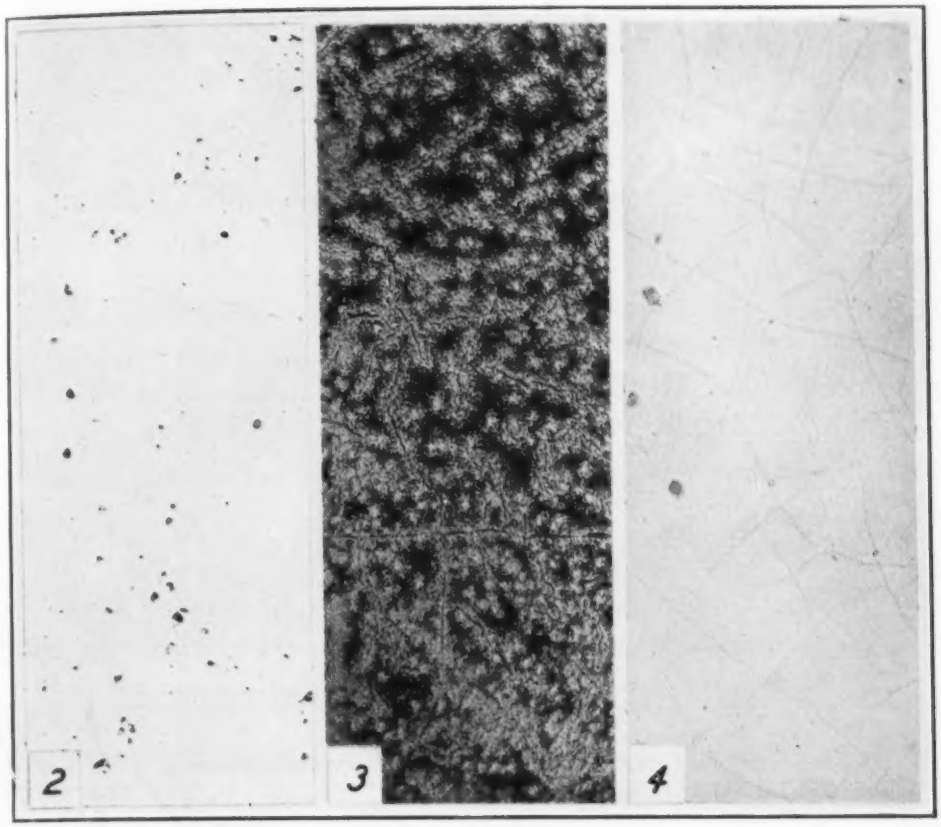

Fig. 2—Microscopic Appearance of Chromium Plate Unetched. × 100.
Fig. 3—Microscopic Appearance of Chromium Plate Etched. × 100. Note the network of cracks which developed on etching.
Fig. 4—Microscopic Appearance of Heated Chromium Plate Unetched. × 1000. Note network of cracks which developed on heating at 325 degrees Cent. (620 degrees Fahr.)

ing could be obtained. A Vickers machine was next tried. Readings were attempted with the pyramid diamond point but again the values were unreliable due to cracking. The results indicated roughly, however, that the hardness was greater than 500 in equivalent Brinell numbers.

Scleroscope readings were quite inconsistent, varying from 40 to about 75. Microscopic examination revealed the fact that the chromium was cracked more or less at each point where a reading had been made. The higher readings are for this reason the more nearly correct ones.

Scratch-hardness measurements made with a Bierbaum microcharacter with a corundum point gave a scratch 2.0 microns in width. This figure is the average of 13 readings made along different por-

tions of the scratches. The extreme readings deviated 30 per cent from the average, indicating the difficulty in reading and the danger in accepting the results of too few measurements. Most of the readings, however, varied less than ± 10 per cent from the average.

The Mohs hardness of electrodeposited chromium was checked and found to be less than 9, the figure assigned to chromium metal in the various reference books. It could be scratched by a diamond, hardness 10, and by the corundum point, 9, of the Bierbaum apparatus. Topaz, of hardness 8, left a faint scratch while quartz, 7, left no mark. It would seem, therefore, that 8 is the maximum hardness that can be assigned to the hardest form of chromium examined by the author. Higher values may have been obtained on specimens contaminated with carbon.

The Hardness of Chromium Plate as Affected by Heat

It had been noted previously by the author[13] that electrodeposited chromium loses some of its hardness on heating. In order to study this behavior quantitatively, specimens were given the following treatments: one specimen was heated in boiling water for 30 hours, one at 200 degrees Cent. for 24 hours, and others for 12 hours each at 260, 275, 290, 325, 500, 700, 850, and 1050 degrees Cent., respectively. The samples were then mounted in Wood's metal and polished for metallographic inspection. The results of Mohs and Bierbaum scratch-hardness measurements are given in Table II. Each value of the latter is the average of 13 to 16 individual readings,

Table II
Effect of Heating on the Scratch Hardness of Chromium

Temperature of Heating Degrees Cent.	Time Hours	Mohs Scratch Hardness	Width of Scratch Microns
Room	..	8	2.00
100	30	8	1.93
200	24	...	1.93
260	12	...	2.00
275	12	...	2.02
290	12	5.5	3.92
325	12	5.5	4.15
500	12	...	3.93
700	12	...	4.66
850	12	...	4.79
1050	12	4.5	5.50

[13] A Study of Chromium Plating. Engineering Research Bulletin 10, 1928, University of Michigan, p. 68.

usually 3 or 4 readings on a scratch with 3 or 4 scratches used on each specimen. It is felt, however, that scratch widths cannot be accurately expressed closer than 0.1 micron. A reading to 0.01 micron represents accuracy of measurement of 0.00001 millimeter or 0.00000039 inch.

These data are presented graphically in Fig. 5. It is evident that at some temperature between 275 and 290 degrees Cent. (525 and

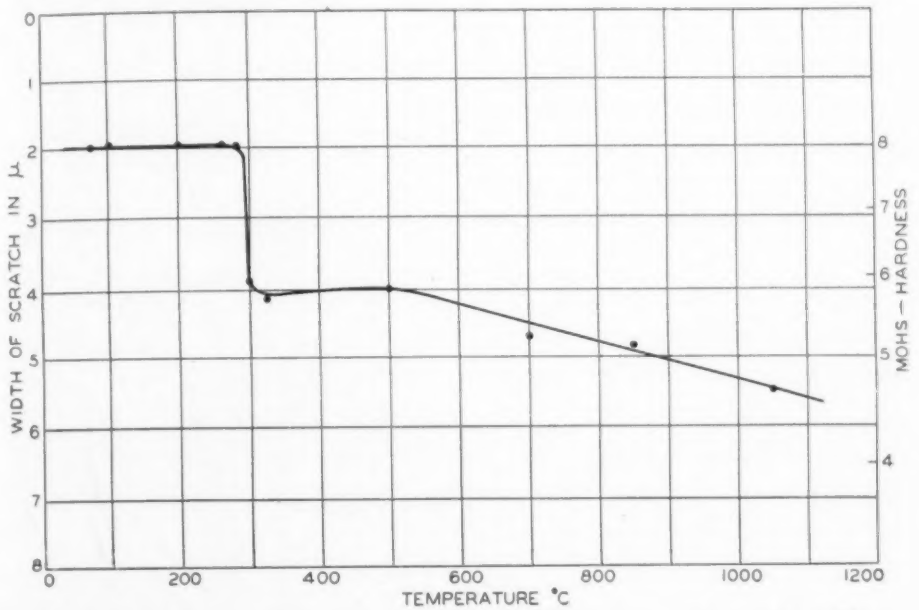

Fig. 5—The Effect of Temperature on the Scratch Hardness of Chromium Plate.

555 degrees Fahr.) a change occurs which causes a sudden drop in hardness from that permitting a scratch width of about 2 microns to one of about 4 microns. Heating and quenching did not restore the original hardness. This change can, therefore, be best explained on the basis of a volatile constituent which is removed at elevated temperatures. The Mohs hardness after heating at the intermediate temperatures, was found to be 5.5; after heating to 1050 degrees Cent. (1920 degrees Fahr.) it was 4.5. One hour's heating at 290 degrees Cent. (555 degrees Fahr.) did not bring about any appreciable softening but after two hours at this temperature the scratch width was 3.87 microns, after 4 hours, 3.92 microns.

Carveth and Curry[14] showed that chromium plate contains over 250 times its own volume of occluded hydrogen which has been con-

[14]H. R. Carveth and B. E. Curry, *Transactions*, American Electrochemical Society, Vol. 7, 1905, p. 140.

sidered by many as the cause of its hardness. It is well known that iron and steel readily occlude hydrogen when cathodically polarized or even upon simple immersion in weak sulphuric acid. The effect on the physical properties is considerable, for Pfeil[15] showed that the elongation of iron was reduced from 60 per cent in the original state to less than 10 per cent when saturated with hydrogen. The effect of the occluded hydrogen is most noticeable in the loss of resistance to impact. In the case of iron the change in hardness is less marked although electrodeposited iron is considerably harder than after annealing. This hydrogen is quite loosely held, probably adsorbed, since Pfeil's results show that mere exposure to the air of a polarized specimen for only a few seconds increased its ductility markedly.

Langdon and Grossmann[16] found that brittleness due to occluded hydrogen could be removed completely by heating at 100 degrees Cent. in air for about 2 hours or at 150 degrees Cent. for 10 minutes. If heated in water at 100 degrees Cent. recovery was accomplished in 10 minutes. Ludwick's[17] results checked these closely.

It is conceivable that the hydrogen in electrodeposited chromium is either, (1) simply adsorbed and loosely bound, (2) present as a solid solution in chromium or, (3) present as a solid solution of chromium hydride in chromium.

Since heating for 30 hours in boiling water or for 24 hours at 200 degrees Cent. (390 degrees Fahr.) did not affect the hardness, it would seem difficult to think of the hydrogen as simply adsorbed. It is most likely present as a solid solution or as a solution of a hydride in chromium. No metallographic evidence could be obtained to indicate which of these hypotheses was the more nearly correct one. The parallel with the behavior of iron is not clear cut because of the difference in grain size and the fact that the penetration of a gas into a metal proceeds preferentially along the grain boundaries.

Hüttig and Brodkorb[18] found a strong evolution of hydrogen gas from electrodeposited chromium when heated above 58 degrees Cent. (137 degrees Fahr.). One would assume that this hydrogen is

[15]L. B. Pfeil, *Proceedings*, Royal Society of London, Vol. 112, 1926, p. 182.

[16]S. C. Langdon and M. A. Grossmann, *Transactions*, American Electrochemical Society, 1920.

[17]P. Ludwick, *Zeit, Ver. deut. Ing.* Vol. 70, 1926, p. 385.

[18]G. F. Hüttig and F. Brodkorb, *Zeit. für anorg. Chemie*, Vol. 144, 1925, p. 341.

very loosely bound. In the present investigation no trace of this type of occluded hydrogen was found because the specimens had been plated at 45 degrees Cent. (113 degrees Fahr.) with the temperature rising at times to 50 degrees Cent. (122 degrees Fahr.). In this manner it is probable that all of the loosely bound or adsorbed hydrogen was removed before examination of the metal was begun.

The grain size after heating to 850 degrees Cent. (1560 degrees Fahr.) was not appreciably different from that in the as-plated condition, hence grain size has little effect upon the increment in scratch hardness represented by the difference between the scratch widths 2μ and 4μ. The grain size is so small that it cannot be discerned readily at 1000 diameters. Any condition of strain due to the process of electrodeposition would have been relieved at least partially upon prolonged heating at 200 degrees Cent. (392 degrees Fahr.). Strain due to the presence of hydrogen in the lattice may, of course, be the fundamental cause of hardness. There is a condition of strain because etching the specimen shown in Fig. 2 develops a network of cracks as shown in Fig. 3. Faint cracking was observed in the specimen heated at 325 degrees Cent., as shown in Fig. 4; this network became progressively more pronounced in samples heated at higher temperatures.

Hardness of Cast Chromium

A specimen of commercial cast chromium made by the Goldschmidt process was annealed for several hours at 1050 degrees Cent. (1920 degrees Fahr.) and cooled very slowly. No analysis was available but the material contained a large amount of oxides and other inclusions visible under the microscope. This material obviously did not contain hydrogen and possessed a fairly large grain size. Any difference in hardness between this sample and the annealed electrodeposited metal would be due, therefore, principally to a difference in grain size and to impurities. Measurements of hardness by means of the Vickers machine gave an equivalent Brinell number of 236. Although the metal was comparatively brittle due to the presence of oxides, a Brinell impression was obtained giving a value of 217. This hardness figure was supplemented by the Bierbaum scratch width of 5.2 microns. The Mohs scratch hardness proved to be less than 5, approximately 4.5.

Another specimen of cast chromium produced by the Electro-

Table III
Hardness Test Results

Material	Bierbaum Scratch Width μ	Mohs Hardness	Brinell
Nitrided Steel	1.3	8.5	730
Chromium Plate	2.0	8	..
Chromium Plate Annealed at 325 Degrees Cent.	4.8	5.5	..
Chromium Plate Annealed at 1050 Degrees Cent.	5.5	4.3	..
Cast Chromium Annealed at 1050 Degrees Cent.	5.2	4.5	150
Platinum	5.4	4.5	70
Armco Iron	6.6	3.3	64
Electrolytic Iron	6.7	3.0	51
Electrolytic Nickel	6.8	3.5	82
Tantalum	7.2	<3.0	..
Copper	9.3	2.8	48
Palladium	9.65	2.8	36
Bismuth	17.3	2.5	35
Magnesium	18.0	2.5	30
Cadmium	25.0	2.0	24
Tin	28.1	2.0	15
Lead	32.2	1.5	8

metallurgical Corporation was tested. This metal was made up of crystals at least 0.5 centimeter in diameter and possessed a brighter luster than the previous specimen. Its analysis was as follows: Silicon 0.35 per cent, iron 0.11 per cent, aluminum 0.71 per cent, and carbon 0.014 per cent. No analysis was made for oxygen. The Mohs hardness was also less than 5 but greater than 4.

The Vickers-Brinell hardness was 150 ± 20. More accurate readings were not possible due to the friability of the metal. It is felt, however, that if electrodeposited chromium were melted in hydrogen and then in a vacuum, the Mohs hardness would probably be at least a half point less or about 4. Electrodeposited chromium contains chromic acid entrapped from the bath which upon heating is changed to chromic oxide. Melting in hydrogen would reduce the oxides. This would place chromium fairly near the curve in Fig. 1.

Comparison of Bierbaum Scratch Width with Mohs Scale and Brinell Hardness

A series of metals was completely annealed in order to remove all chances of strain hardening, of excessively small grain size in the case of electrodeposited metals or of other effects. Bierbaum and Mohs scratch and Vickers-Brinell hardness measurements were made. Electrodeposited chromium in various stages of anneal was also tested. The purity of the materials in all cases was the highest obtainable. The analysis for the cast chromium specimen has already been given. The results of tests are given in Table III.

Fig. 6 presents these data graphically. There seems to be some relationship between the scratch hardness as measured by the Mohs scale and that measured on the Bierbaum apparatus. Since Mohs hardness cannot be determined very closely the points have been put in as lines one-half hardness unit in width indicating limits of error

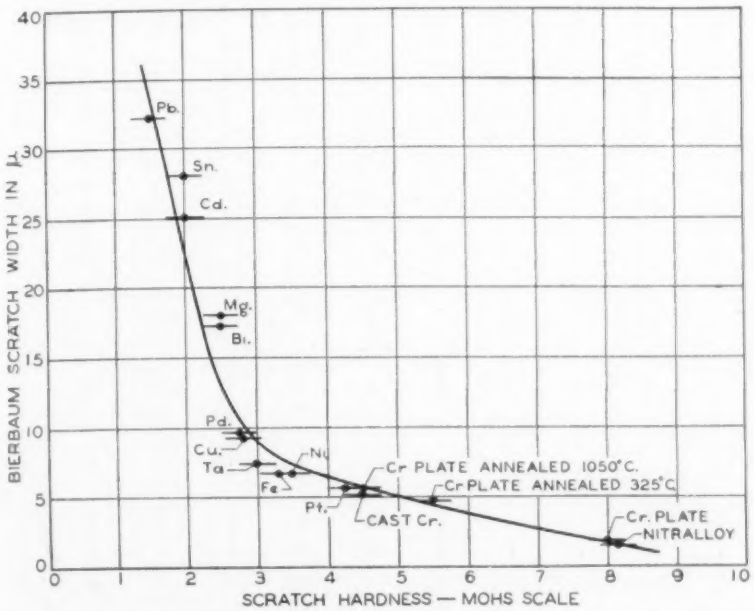

Fig. 6—Relationship Between the Mohs and the Bierbaum Scratch Hardness of Annealed Metals.

of $\pm$ 0.25 of a Mohs hardness unit. The relationship is fairly satisfactory when the arbitrary manner in which the Mohs scale was originally arrived at is taken into consideration.

The curve Fig. 7 giving the relationship between scratch width and Brinell hardness, however, seems less justifiable. But scratch width will impart an idea of the comparative hardness of material only to the mineralogist and physicist, and it carries no significance to a metallurgist who is familiar with Brinell or Rockwell values. There are no data on any accurate relationship between scratch hardness and hardness measured by indentation methods, and it was thought that some fair approximations might be reached which would be valuable. For this reason a specimen of nitrided steel was tested for hardness with both the Bierbaum apparatus and the Vickers hardness testing machine, the value of the latter being readily convertible to Brinell numbers.

A specimen of commercially nitrided steel about 2.5 centimeters

long was surface-ground with a standard 3-degree bevel so that one end had the original surface while the other end had been ground off well into the softer core. The piece was placed in a chuck which was provided with a sliding base that could be moved rectilinearly through a definite distance by means of a calibrated screw. Vickers

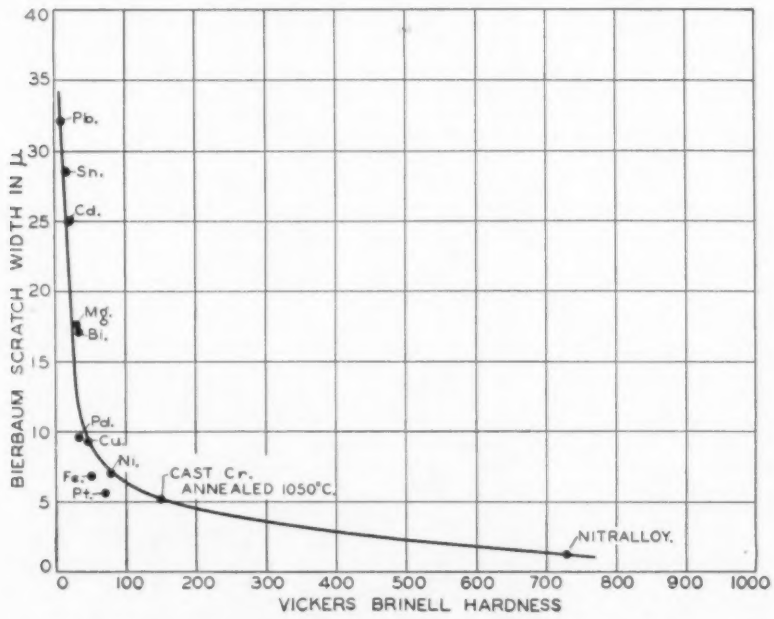

Fig. 7—Relationship Between the Bierbaum Scratch Width and the Vickers-Brinell Hardness of Annealed Metals.

impressions were made with the pyramid diamond point and then Bierbaum scratches were made near and parallel to these impressions. The scratch width was measured opposite each impression. Table IV gives the Vickers-Brinell and the Bierbaum data side by side.

By plotting these values against each other as shown in Fig. 8, a curve is obtained which shows the relationship of these two types of hardness values for nitrided steel.

Comparison with the Bierbaum-Brinell curve in Fig. 7 shows that the relationship existing for annealed materials does not hold for heat treated or worked steel. This is further brought out in testing two samples of KA2, an iron alloy containing 18 per cent chromium and 8 per cent nickel. In the cold-rolled condition the scratch width was 9.8μ and the Brinell hardness 360; a cast sample of almost identical composition had a scratch width of 7.4μ but a Brinell number of only 150. These results conform with the general opinion that no

Table IV

Comparison of Vickers-Brinell Hardness with Bierbaum Scratch-Width of Nitrided Steel

Reading	Vickers-Brinell Numbers	Width of Scratch
1	730	1.30
2	693	1.47
3	653	1.80
4	609	1.82
5	550	2.21
6	528	2.25
7	499	3.78
8	469	4.03
9	424	4.50
10	351	6.28
11	306	6.48
12	260	6.72
13	242	7.79
14	224	8.43
15	223	8.48

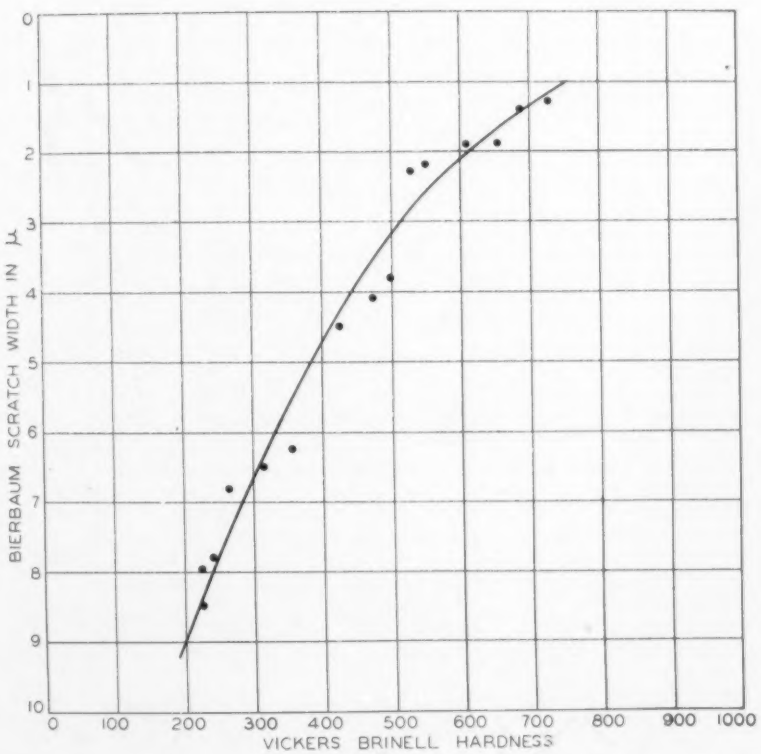

Fig. 8—Relationship Between the Bierbaum Scratch Width and the Vickers-Brinell Hardness of Nitrided Steel.

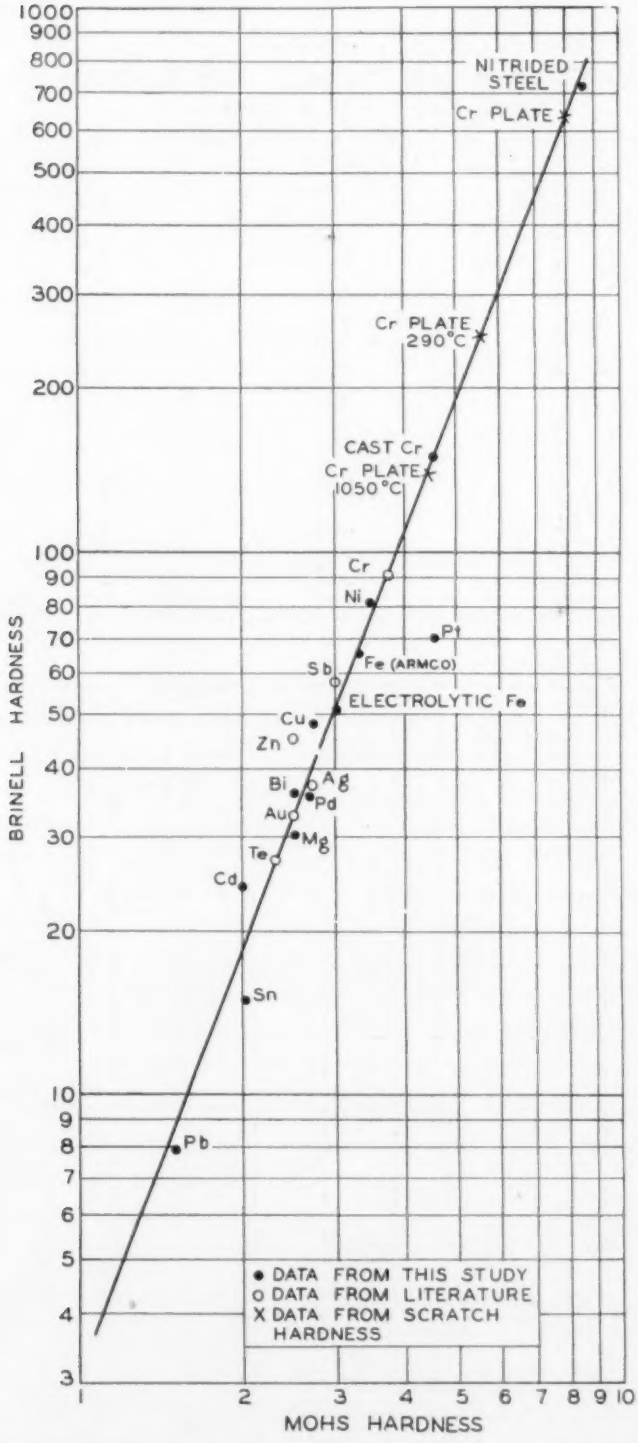

Fig. 9—Relationship Between the Mohs Hardness and Brinell Hardness of Annealed Metals.

reliable approximations of the Brinell hardness of chromium plate can be drawn from the Bierbaum scratch hardness data.

Fig. 9, plotted on log-log paper, shows close agreement between Mohs hardness and Brinell hardness within the range investigated. The probability of the accuracy of this curve is increased by the addition of some points where the Mohs hardness has been obtained from Landolt-Börnstein and the Brinell values from the work of Edwards. It is not within the scope of this paper to attempt to establish definite relationships between hardness obtained by various methods. This portion of the work was done merely to arrive at an approximation of the Brinell hardness of electrodeposited chromium, a figure which should be of much greater interest to a metallurgist than scratch hardness values.

A study of this curve leads to the conclusion that electrodeposited chromium has an equivalent Brinell hardness number of between 600 and 650 in the as-plated condition. After annealing at about 290 degrees Cent. (555 degrees Fahr.) which presumably removes hydrogen of solid solution, the Brinell equivalent is approximately 250. Fully annealed chromium plate is softer than the samples of cast chromium which were available. This is true most probably because of its greater purity. The hardness value was found to be in the neighborhood of 135 Brinell.

Conclusions

The results of the study on the hardness of chromium can be summarized in the following table.

Material	Treatment	Hardness		
		Mohs	Bierbaum Scratch width Microns	Brinell
Chromium	Value from literature	9	....	...
Chromium plate	None	8	2.00	625*
Chromium plate	Heated at 325°C.	5.5	4.15	250
Cast Chromium	Annealed at 1050°C.	4.5	5.20	150
Chromium plate	Annealed at 1050°C.	4.5	5.50	135*
Chromium plate	Melted in hydrogen	3.8*	....	89
	Value from literature			

*Calculated values.

It is believed that the difference between the Mohs hardness of 9 ascribed in the literature to chromium and 4.5 determined for cast chromium in this study may be due to possible carbide impurity in the specimens on which the former value was obtained.

The loss in hardness of electrodeposited chromium upon heating above 290 degrees Cent. (555 degrees Fahr.) is due to the removal of

hydrogen of solid solution at that temperature. The further softening effect upon heating up to 1050 degrees Cent. (1920 degrees Fahr.) is probably due to the removal of internal strain and to grain growth. Annealed cast chromium was found to be slightly harder than annealed electrodeposited chromium. The presence of impurities in the former is most likely responsible for this difference.

DISCUSSION

Written Discussion: By W. Blum, chemist, Bureau of Standards, Washington, D. C.

These results for the hardness of chromium as measured by different methods are of considerable scientific interest. Their practical application is less certain. The "hardness" of electrodeposited chromium is especially of interest in connection with wear-resistance. Unfortunately there is no simple relation between any hardness measurements and resistance to wear. To the extent that the latter involves abrasion, it is at least probable that the scratch-hardness is a better criterion than the Brinell hardness. It is doubtful therefore whether the author's assumption that "Brinell hardness . . . should be of much greater interest to a metallurgist than scratch-hardness values," applies especially to chromium plating.

Even the scratch hardness is not an accurate indication of wear-resistance. For example, in recent experiments H. K. Herschman[1] found that chromium plated gages that had been heated for 24 hours to 300 degrees Cent. were much more resistant to wear than unheated gages, although we would expect the heated gages to be "softer," as reported by Schneidewind. Evidently other intangible properties such as "toughness" have a marked influence on wear-resistance.

The unheated specimens of Herschman yielded a scratch width of about 2 microns, i. e., about the same as those of Schneidewind. However, Herschman observed *no decrease* in scratch hardness after heating to 300 degrees Cent. That hydrogen is evolved as low as 200 degrees Cent. is indicated by the marked increase in the cracking of the heated deposits, as shown in a paper now in press in the Journal of Research.[2] It is at least probable that relatively small differences in the conditions used in the plating or the heating might change the temperature at which a sudden drop in hardness occurs. Evidently more critical experiments will be required to fully explain the form and behavior of hydrogen contained in electrodeposited chromium. In any such study the data of this paper will be helpful.

Written Discussion: By Christopher Bierbaum, vice-president, Lumen Bearing Co., Buffalo.

[1] "The Resistance of Chromium-Plated Gages to Wear." Research Paper No. 276. Bureau of Standards Journal of Research, Vol. 6, p. 295, 1931.

[2] "The Porosity of Electroplated Chromium Coatings," W. Blum, W. P. Barrows and A. Brenner. Research Paper U. S. Bureau of Standards.

The superiority of the Vickers diamond pyramid testing machine over the original Brinell is entirely due to the fact that any indentation made by the Vickers machine is always symmetrical to every other indentation, regardless of load. This is not true with the standard Brinell and in order to overcome this difficulty, at least in a measure, two different Brinell scales are in use. In the microcharacter tests the same thing is true as in the Vickers, in that the continuous indentation at any one point is strictly symmetrical to that at all other points, the only difference being that in the Vickers the load is normal to the test surface, whereas in the michrocharacter the load is the resultant of two forces, the static weight upon the jewel point and the horizontal pull, producing a resultant that makes an angle of 35.25 degrees with the normal to the test surface.

In general, for all testing methods where the hardness is determined by an indentation, the mathematical expression for such hardness is derived from the ratio of the load to the area loaded, and since areas are directly proportional to the square of their homologous sides, the squares of lineal dimensions of such indentations are used. In a Vickers test the loaded area is directly proportional to the square of the diagonal of the indentation; in like manner, in the microcharacter test the loaded area at any point is directly proportional to the square of the width of microcut. Why the author should have used the width of cut rather than a factor of its square, is not at all apparent, except, perhaps, that this fallacy was first introduced by the Bureau of Standards.

From work done, it seems altogether likely that a fairly approximate scale can be developed according to which microhardness can be expressed in terms of Vickers Brinell. It cannot, however, be done satisfactorily in a manner the author proposes from the data in Table IV and plotted in Fig. 8. In order to produce a truly relative scale, it will be necessary, in the first place, to express both Vickers and microhardness in corresponding terms; that is, in terms of the ratio of load to area loaded; and, secondly, each determination with the Vickers must be made upon a homogeneous material, which was not done in the author's work. It is impossible to make a determination with Vickers upon a nitrided surface of nitralloy steel without bringing into effect several successive layers of different degrees of hardness, owing to its depth of penetration. The value of expressing hardness in terms of a definite and exact standard is certainly of more importance than an expression in relative approximations of different standards since, "The word *hardness* of a metal is used to express five ideas."[3]

When making microhardness tests upon a pure metal, especially so when it exists in a soft annealed state, the property known as anisotropy must be taken into consideration. Tests made upon a metallographic surface show a difference of microhardness at any one point, depending entirely upon the direction in which the cut has been made; this anisotropic effect is due entirely to atomic orientation. In testing pure annealed copper the microhardness at any point may be twice as high if cut in one direction as it would be had it been cut in some other direction and for chemically pure zinc this difference may be

[3]General Metallurgy—Hoffman, 1913, p. 9.

as high as four to one.[4] For the foregoing reason the microhardness or the width of cut for the different pure annealed metals cannot be expressed in terms of single numbers; the designation should carry with it either maximum, minimum or average. Therefore, the figures for such metals as given in Table III and Fig. 7 cannot be regarded as reasonably accurate.

For the first instruments, the artificial leuco sapphire was used, it being the most serviceable jewel that any lapidarian, up to that time, has been able to grind with the requisite degree of accuracy. The author mentions a corundum point as being used in the microcharacter; if he had a full appreciation of the relative serviceability for this purpose of the artificial sapphire as compared with corundum, he might have been more accurate in his use of terms. Corundum, no doubt, serves well for a Mohs scratch hardness test but when the exacting requirements for a keen edge and point of a cutting jewel are considered, the most serviceable aluminum oxide product is the pure aluminum oxide artificially prepared, and even this has now been completely abandoned for the diamond. The Mohs scale of hardness is very essential for a prospecting mineralogist in the field; but what contribution this crude and approximate scale can make to modern refinements on hardness study is altogether obscure; it seems but to lead to vagaries and inconsistencies.

The relative hardness of nitrided steel and chromium plate, as given in the author's Table III, is inconsistent and manifestly in error. 730 Vickers Brinell hardness on a nitrided nitralloy steel surface does not correspond to a microcut of 1.3 microms in width, this reading should have been more nearly 2.4 microms. The reading given for chromium plate as 2.0 microms is by no means the hardest electrolytic chromium plate.[5] The hardest chromium plate is appreciably harder than the hardest layer of a nitrided steel surface of 920 Vickers Brinell.

The author's discovery, that chromium plate softens when heated and annealed at a temperature between 525 and 555 degrees Fahr., due to the elimination of occluded or adsorbed hydrogen, as shown in Table II, Fig. 5, and Table III, would certainly be a beautiful law. Unfortunately, however, it exists as pure fancy only, it has no existence in fact. Chromium plate, when heated and annealed in a manner specified, does not soften. Investigations in the laboratories of the Lumen Bearing Co. show, without a single exception, that the process of successive and prolonged heating and annealing chromium plate does not produce a softening effect.

Written Discussion: By W. E. Jominy, research laboratories, A. O. Smith Corp., Milwaukee.

The hardness and behavior of chromium plate under various conditions is a matter of concern to many industries. We are indebted to Mr. Schneidewind, who is well known in the field of chromium plating, for giving us further information on this subject.

Mr. Schneidewind's findings would indicate that at temperatures of 525 degrees Fahr. and below, we may expect chromium plate to offer good re-

[4] *Transactions*, American Institute of Mining and Metallurgical Engineers, 1923, p. 980.

[5] TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 1009.

sistance to wear, but when this temperature is exceeded, less satisfactory performance may be expected. From these results, one would expect satisfactory performance of chromium plating on the large metal rolls used in the paper industry, which operate at around 400 degrees Fahr., but questionable performance when used on forging dies where surface temperatures are very high. Actual experience with both of these applications have been in accordance with this postulation.

In connection with the fine cracks which appeared in the chromium plate after heating to 620 degrees Fahr., I should like to inquire whether these cracks are due to the difference in linear expansion of the chromium plating and the metal on which it was deposited, or whether the chromium was removed from the base metal before heating. Have similar cracks been found when the thickness of the chromium deposit was around 0.001 inch or less?

The relationship between the hardness of the metals as indicated on Mohs scale and the quotient of the specific heat divided by the coefficient of linear expansion, as shown in Fig. 1, is quite interesting. Although relationships of this kind are discussed in *"Science of Metals"* by Jeffries and Archer, it is perhaps not so well known among metallurgists that there is an approximate relationship between the coefficient of linear expansion and hardness of metals. If the coefficient of linear expansion values for the metals given in Table I of this paper are plotted against the Mohs hardness values, a fair relationship will be found. If Mr. Schneidewind's corrected hardness values for chromium, iron, and palladium are accepted, then only three metals will be found which are more than 0.5 points off this curve. These three metals are ruthenium, manganese, and arsenic. Two of them, ruthenium and manganese, are likewise off the curve in Fig. 1 of Schneidewind's paper, although ruthenium does not appear to be off because of an error in calculation occurring in Table I. This would indicate that further tests of these two metals should be made. Work of this type is very worth while, and it is to be hoped that Mr. Schneidewind will continue these studies.

Written Discussion: By A. B. Kinzel, associated with the Union Carbide and Carbon Research Laboratories, Long Island City, N. Y.

Mr. Schneidewind is to be complimented on presenting a paper on a subject in which there is so much interest. The problem to which he set himself, is a most difficult one as the scales used are purely relative and arbitrary.

Mr. Schneidewind has worked on chromium plate produced under one set of conditions. Whether or not variation in the conditions of deposition would vary the hardness of the case may be considered as problematic but must certainly be taken into consideration in attempting to assign a specific Brinell value for the hardness of chromium plate. This value is arrived at by comparison with other materials, more particularly nitralloy as tested by Vickers hardness and the Bierbaum microcharacter. We find it peculiar that the hardness obtained by the Vickers machine on the nitralloy specimen used by Mr. Schneidewind is only 730 Vickers Brinell. Either this is an error, or the nitriding was far from representative. If the case was far from representative, then the conversion from the Vickers number to Brinell is inaccurate. Moreover, the hardness of the nitrided case is not uniform throughout the depth of the

case. Thus, in making a Vickers impression, integrated values are obtained, depending upon the hardness gradient. It may well be that the immediate surface is extremely hard, so that with the microcharacter a relatively small width of scratch ensues and still a low Vickers reading results due to lack of hardness immediately under this layer. Thus, it seems to us that the very standard by which Mr. Schneidewind attempts to assign an arbitrary value to the hardness of chromium plate is false. We further believe this standard to be unreliable, in that it assumes the Vickers-Brinell relation, which is purely empirical. It is hardly to be expected that a definite relation between different types of material may be obtained when using a pyramid indenter on the one hand, and a sphere on the other. Much more logical is the use of a diamond ball as in the Monotron, where the various factors entering into the Brinell formula are definitely set.

The use of the microcharacter itself under the conditions described by Mr. Schneidewind is open to question, as a sapphire is used instead of a diamond. It is well known that in testing chromium plate with a sapphire on the microcharacter, wear ensues and corrections for this must be made. The omission of any reference in Mr. Schneidewind's paper to wear of the sapphire and to any correction is unfortunate. A statement as to the weights used in the scratch tests should also be incorporated. We find that a 3-gram weight gives a scratch width on chromium plate insufficient for accurate measurement. Thus, simply on the score of the microcharacter method as used, the hardness value assigned to chromium plate is open to serious question. It may be remarked at this time that Mr. Bierbaum has reported chromium plate which cannot be scratched with a sapphire. This throws still further doubt on the use of a sapphire in measuring the hardness of chromium plate.

The correlation of Mohs hardness with Brinell is also open to question. The Mohs hardness scale is such that the relative value of a number at one end of the scale such as between 3 and 4, and one at the other end such as between 9 and 10, may be vastly different. It is significant that in scratching chromium plate with a diamond, the diamond is also scratched. I doubt if there is very much relation between Brinell hardness and Mohs scratch hardness, and in this connection I am reminded of a story which I believe is due Mr. Archer. It was found that iron tools used for removing aluminum punchings from the press scratched the aluminum, the Brinell hardness of the tool being greater than that of the aluminum. Accordingly, iron tools were made with Brinell lower than that of the aluminum, and the scratching continued just the same. Aluminum tools were then used, and it was found that even though the hardness of the aluminum tools used was more than that of the iron tools and greater than that of the aluminum part which was being handled, no scratching resulted. The lack of relation between scratch and indentation hardness is strikingly illustrated.

We feel that a very great deal of work is necessary before a Brinell value may be assigned to chromium plate, and that the 625 Brinell of the author is misleading. Indications from comparisons between diamond ball indenters and diamond scratch hardness place the average value at something above 1000 Brinell. We trust that the author will carry on his work with more reliable

standards and feel sure that if he does so he will find that the average Brinell value of chromium plate is more in accordance with what would be expected from common experience in service.

Oral Discussion

A. H. D'ARCAMBAL:[6] Chromium plating is being used more and more by industry so we are always much interested in any papers on this subject. We would like to ask the author a few questions:

1. Is there any advantage to drawing a chromium plated part such as a cylindrical plug gage to 200 degrees Cent. for say 24 hours considering that this drawing treatment has no effect on the original hardness?

2. It is now common practice of automotive concerns in the case of plated parts such as radiator shells, etc., to draw these parts to 450 degrees Fahr. in oil so as to resist corrosion to a greater extent. What is the answer to that? Why does this drawing treatment result in greater resistance to corrosion?

3. At times we flash-plate parts in a solution of a different gravity than the solution used for the so-called heavy plate. Would the flash-plate say of a few ten thousandths in thickness be of approximately the same hardness as a heavier plate? Some claim the hardness is the same, others that one is harder than the other. Is the author in a position to answer this important question?

W. J. MERTEN:[7] This paper seems to be of some value aside from the consideration of chromium plating and its hardness. Scratch methods for determining hardness of materials is particularly of value in the so-called extremely hard water-quenched and tempered rolls for determination of their resistance to wear and performance in service. The rolls are used in the cold rolling of stainless steel strip and other difficult rolling materials. The author has established at least some comparative figures which do seem to me worthy of consideration. The Bierbaum value or the microcharacter scratch is the only measure whereby hardnesses of 106 or 108 scleroscope values can be effectively handled, and a comparison with other scales does seem to be essential to the intelligent interpretation of that scale.

A definite formulation of values, at least to some degree comparative with the generally accepted values of hardness, is certainly to be welcomed by members of the society who are particularly interested in parts that do not permit indentation measurements to be made upon the surfaces. I have particularly in mind the polishing of roll surfaces to a degree of perfection to permit the retention of mirror polish on material, produced during cold rolling on subsequent forming operations for automotive parts, etc. The polishing and buffing operations of hard rolls do seem to introduce a flow of metal which apparently renders the skin of the rolls soft and the width of the scratch in the curved surface of the rolls is very much greater as compared with the original hardness prior to buffing and after the grinding operation.

I think that we should consider this paper from the viewpoint of the man who is in actual need of at least some rough measure of comparison with figures of the present methods of hardness measures.

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[6]Metallurgist, Pratt and Whitney Co., Hartford, Conn.

[7]Associated with Lyon, Inc., Asbury Park, N. J.

C. B. SADTLER:[8] The author of this paper has brought up some very timely points, and several of those who discussed the paper have emphasized the more important of those points, particularly the last speaker, Mr. Merten, who has indicated the difficulties that arise in grinding hardened steel. It is quite well known that a soft layer will result at times, and the methods of hardness measurements employing loads in excess of a few kilograms are, generally speaking, inadequate to show such softness. There are, however, types of hardness testers that have been recently developed and offered for use which will show the hard, or for that matter, the soft superficial condition; that is, will give a measure of the hardness of an extremely thin layer, be it harder or softer than the underlying layers. While I do not want to appear as leaning too strongly towards any particular make of machine, I do not know how to avoid some of that, so I will mention specifically the Monotron tester which permits of varying loads from a few kilograms up to 160 kilograms, which loads may be applied on a diamond indenter of spherical shape. With such a shape, as is also true of the much older type of steel ball Brinell, there is a linear relationship between the depth of impression and the load applied on uniform material. That can be very conveniently demonstrated at any time by a very simple manipulation of the Monotron. In the case of the Vickers test, due to the shape of the diamond indenter, there is a different geometric relationship. It is a simple one, however, as is claimed by the makers of the machine and as we have verified on a number of occasions. There is a direct relationship between the hardness numeral, which is kilograms per square millimeter of impression, (the same unit used in the Brinell), and the load, from a small fraction of one kilogram up to 50 or 60, providing the material is uniform. The numerical values often vary less than one per cent which is much better than many other types of commercial testing.

This brings me to the point at which I started, as to the manner in which thin surface layers of material can be measured when the underlying material is of different hardness. We have abandoned the microcharacter, at least for the time being. We have had it for over a year, and have done only enough work on it to assure ourselves that the agreement was so disappointing as to discourage further use. Because we desired to study the hardness of these thin layers, we investigated the use of the Vickers diamond, which, by the way, is relatively inexpensive. You can buy several of them for the price of one microcharacter diamond and you can have one relaped for almost a nominal cost. By means of a special attachment we have used loads as low as one-tenth of a kilogram; I will express myself in terms of kilograms so you can keep in mind the order of magnitude which, as you will recall easily, is a very small fractional point of the standard load for the Rockwell C, which is 150 kilograms. So then with these values of tenths of a kilogram we are in a position to measure these thin layers which include chromium plate. We have been most successful in using loads of a few tenths of a kilogram in measuring chromium plate and can measure quite thin layers. We have found limiting thickness values where the underlying material, be it real soft material or be it hardened steel, exerts no appreciable influence on the hardness value. In con-

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nection with these lighter load Vickers tests, the impressions, while not as clearly cut and as capable of close and exact measurement as are the larger and more common impressions, they still permit of reproduction of results to, I would say roughly, 1 part in 50, which I think you will agree is much closer than many of the hardness measurements which are made at the present time.

Author's Closure

It would appear from the discussion that many people believe that resistance to wear of chromium is due to only its hardness. It is very possible, however, that the low coefficient of friction also plays an important part. Tests have been made at the University of Michigan with unlubricated bushings on chromium plated shafts. When a bushing "froze" to a plain steel shaft a quantity of tightly adherent metal was found on the shaft, which was removable only with emery cloth. On a chromium plated shaft, the worn-off metal would be found in a powdery condition capable of being blown off or wiped off with a cloth.

In regard to Mr. Bierbaum's discussion, we believe that all of Vickers readings were made upon material which was homogeneous and that Vickers hardness is sufficiently accurate for nitrided steel since it has been standardized upon by many plants. The anisotropy of chromium hardly enters into consideration in our measurements since all of the scratches were taken parallel to the plating surface or, in other words, perpendicular to the direction of plating. The measurements, furthermore, check those of Grant and Grant and of the Bureau of Standards. It is true that the Mohs scale of hardness is not as capable of refinement as the microcharacter, but Goldschmidt, in his work on hardness, has compared hardness with the closest distance between the atoms and used the Mohs scale. In order to do this he found standards by which he was able to obtain hardness within $\frac{1}{10}$ of a point. It is unfortunate that Mr. Bierbaum is not agreed with our readings as the hardness of nitralloy. This was an especially soft specimen but was in the range comparable with our chromium plate.

In response to Mr. Jominy's question as to the cracks found upon heating, they are not due to the difference in expansion of the chromium and of the base metal because we pointed out on page 120 of the paper the backing was dissolved away before heating.

This is in answer to Mr. Kinzel's discussion. The chromium plate described in this paper was produced under commercial conditions. It is very possible that if plated from a tri-valent chromium bath the hardness might be different. At any rate, the hardness of these specimens check the findings of Grant and Grant and of the Bureau of Standards. The specimen of nitralloy reported upon was especially soft. It had been in contact with superheated steam at 1100 degrees Fahr. for 2000 hours. It was selected because its hardness was closer to that of the chromium plate than normal nitrided specimens.

No reference has been made as to wear of the sapphire in the microcharacter. It may be pointed out, however, that the instrument is comparatively new. A few hardness measurements on brass have been made before using it for chromium. The three gram weight, the only one supplied with

the instrument, was used, making the results comparable to those of Grant and Grant and of the Bureau of Standards. Although chromium plate, incapable of being scratched with the sapphire, may have been reported, the present author has not found any which could not be scratched slightly with a topaz. The author agrees with Mr. Kinzel that microcharacter readings are not related in all cases with Brinell hardness values. It is pointed out in the paper that the scratch hardness measurements do not show the results of cold work. It is believed, however, that there is a relationship between scratch and indentation hardness of metals in the fully annealed condition.

In answer to Mr. D'Arcambal:

1. Drawing a chromium plated plug gage to 200 degrees Cent., is advantageous in preventing cracking. This is especially true if the piece contains severe quenching strains. Hydrogen embrittlement due to plating along with these quenching strains might result in cracking. The author once plated a heat treated belling tool which cracked completely across within two days after plating. A 200-degree Fahr. draw might have prevented this.

2. A theory explaining the greater resistance to corrosion obtained by drawing chromium plated radiator shells to 450 degrees Fahr. is not advanced. It might be due to a change in the potential of chromium caused by hydrogen or to a change in the internal strains of the chromium plate.

3. Flash-plate is often made in a solution of different gravity than hard plate because for flash plating one wants greatest throwing power. When making hard plate the operator is willing to sacrifice throwing power and use specially-shaped anodes. The author believes that the flash-plate is of the same hardness as the thicker plate but due to its extreme thinness the apparent measureable hardness is more affected by the properties of the underlying material.

We regret that some of the commentors have not observed softening upon hardening chromium plate. After determinations such as described in the paper, we have observed hardness changes so apparent that whereas the original sample would not be filed, the heated sample could readily be scratched with a common jack-knife. The specimens are at the University of Michigan and we will be glad to offer them for the inspection of any one interested.

CHARACTERISTICS OF ALLOYED CAST IRON

By F. W. Shipley

Abstract

Increased quality which is reflected through higher valve seat hardness and improved microstructure can be obtained by additions of nickel and chromium to automotive-type cylinder iron. Different combinations of these alloys were used and it was found that a ratio of three parts of nickel to one of chromium gave the greatest improvement in structure in conjunction with maximum hardness. Effect of prolonged heating on three representative plain irons as well as on three nickel-chromium-alloyed irons of the same base composition is also shown and here again a marked difference is revealed in favor of alloyed irons. A method of producing chilled roller wheels by additions of chromium instead of special cupola charges is given. This process is capable of more perfect control and at the same time produces a superior product.

THE history of the development of iron for internal combustion engines is one involving the progressively increasing demands of industry for better quality, improved structure and greater wearing properties because the modern trend is toward smaller but more powerful engines, higher compression, higher speeds, more cylinders per block and increased combustion temperatures. These requirements having exhausted the ordinary resources of the production foundry, it was natural to turn to other available means of improving cast irons, thus the use of alloying elements was a consequence.

For the purpose of determining some of the qualities which might be obtained through the use of alloys, the research work described in the present paper was conducted. As each problem was a separate and distinct one in itself, they are given separately. The author, however, wishes to point out that it has not been his intention to purposely omit any one alloy from this work, but rather on account of lack of time, to investigate only those which have come into more general use in the last decade.

A paper presented before the Thirteenth National Metal Congress held in Boston, September 21 to 25, 1931. This paper was secured by the A. S. S. T. but transferred to the technical program of the Society of Automotive Engineers, Wednesday, September 23, 1931. The author, F. W. Shipley, is a member of the A. S. S. T. and is foundry metallurgist with the Caterpillar Tractor Co., Peoria, Illinois. Manuscript received June 20, 1931.

Effect of Additions of Chromium and Nickel on Hardness and Structure of Cast Iron for Automotive Engines

Due to the difficulties encountered with wearing of valve seats of automotive engines and uneven wear of the cylinder bore itself, an attempt was made through the use of alloys to increase the hardness and density of the structure beyond a point which had previously been considered safe for machineability. Earlier attempts to accomplish this through lower silicon content and increased steel content had resulted only in machining difficulties due to white or mottled sections in thin parts of the castings.

In an experimental study of this problem five six-cylinder motor blocks were poured from each ladle containing compositions Nos. 1 to 5 of Table I. It is to be noticed that the silicon content in the regular iron was lowered from 2.34 per cent to approximately 2.10 per cent in those charges to which the alloys were to be added.

The purpose of this investigation was to study the hardness and chilling effect obtained by increasing the chromium content in increments of 0.10 per cent while the nickel content remained the same. This, then, would determine just what ratio of nickel to chromium would be necessary to prevent machining difficulties. The theoretical mixture, however, was not obtained in the case of Mixture No. 2.

The physical values obtained from test bars which were poured from these ladles, as well as the Brinell hardness numbers taken at the valve seat of the cylinders are given below.

No.	Transverse 1¼-12 Inch Stress-Pounds	Transverse 1¼-12 Inch Deflection	Tensile Strength Pounds per Square Inch	Avg. Brinell Hardness Number of 5 Cylinders
1	3025	0.130	28,400	163
2	3120	0.119	29,000	171
3	3560	0.150	30,100	178
4	3650	0.122	35,270	189
5	3100	0.131	29,660	162

One cylinder selected as the average of each group was sectioned longitudinally through the bore and Brinell readings were taken from the head contact face down at intervals of approximately 1½ inches. These results are as follows:

	1	2	3	4	5
	167	184	198	227	179
	177	177	187	190	143
	170	170	198	198	141
	164	170	184	194	141
	177	177	181	196	137
	174	178	202	198	163
	177	190	184	221	181
Average	172	178	191	203	157

It is significant that cylinders of Mixture No. 1 with a 2.05 per cent silicon and 3.45 per cent total carbon having a 3 to 1 nickel-chromium ratio gave a variation of 13 points Brinell hardness. Mixture No. 2 with practically the same base but a 2.75 to 1 nickel-chromium ratio showed a variation of 20 points Brinell hardness. Mixture No. 3 having virtually the same analysis as No. 1 except that the nickel-chromium ratio is 2 to 1 gave a difference of 21 points Brinell hardness. Mixture No. 4 is practically the same as Mixture No. 2, but with a 1.25 to 1 nickel-chromium ratio gave a difference of 37 points Brinell hardness. Mixture No. 5—the plain iron—showed the maximum difference of 44 points hardness. Mixture No. 2 gave a 6-point higher average hardness than No. 1 but this is due to the 13 points lower total carbon.

It will be noted that the hardness is quite uniform over each lot of alloyed iron cylinders as well as over the bore of the sectioned cylinder. In each case a decrease in hardness occurred at the junction of the water jacket wall with the cylinder wall, but this difference was not so pronounced in the case of the alloyed irons. One might infer that Mixture No. 4 would be ideal from a hardness standpoint, however Mixture No. 1 showed the least variation. This is usually true of the 3 to 1 nickel-chromium ratio.

The problem then would seem to be one of improving Mixture No. 4 so that a uniformly high degree of hardness would result. This can be done by raising the nickel content to approximately 1.00 per cent, thus obtaining an ideal iron for heavy duty cylinder work.

Figs. 1 to 10 illustrate the structures prevailing in the cylinder casting specimens examined. The details of their structures are described in the captions.

Mixture No. 2 is the best "soft" iron of the lot. It consists of

Table I

	Mixture			Alloy Iron Analysis						
No.	Per Cent Pig Iron	Per Cent Scrap Iron	Per Cent Steel	Total Carbon	Silicon	Phos-phorus	Sulphur	Man-ganese	Nickel	Chro-mium
1	35	50	15	3.45	2.05	0.180	0.095	0.60	0.53	0.14
2	35	50	15	3.32	2.05	0.184	0.096	0.61	0.41	0.15
3	35	50	15	3.43	2.11	0.185	0.095	0.63	0.51	0.25
4	35	50	15	3.34	2.07	0.190	0.094	0.62	0.49	0.37
				Plain Iron						
5	35	50	15	3.30	2.34	0.190	0.090	0.64	0.05	0.09

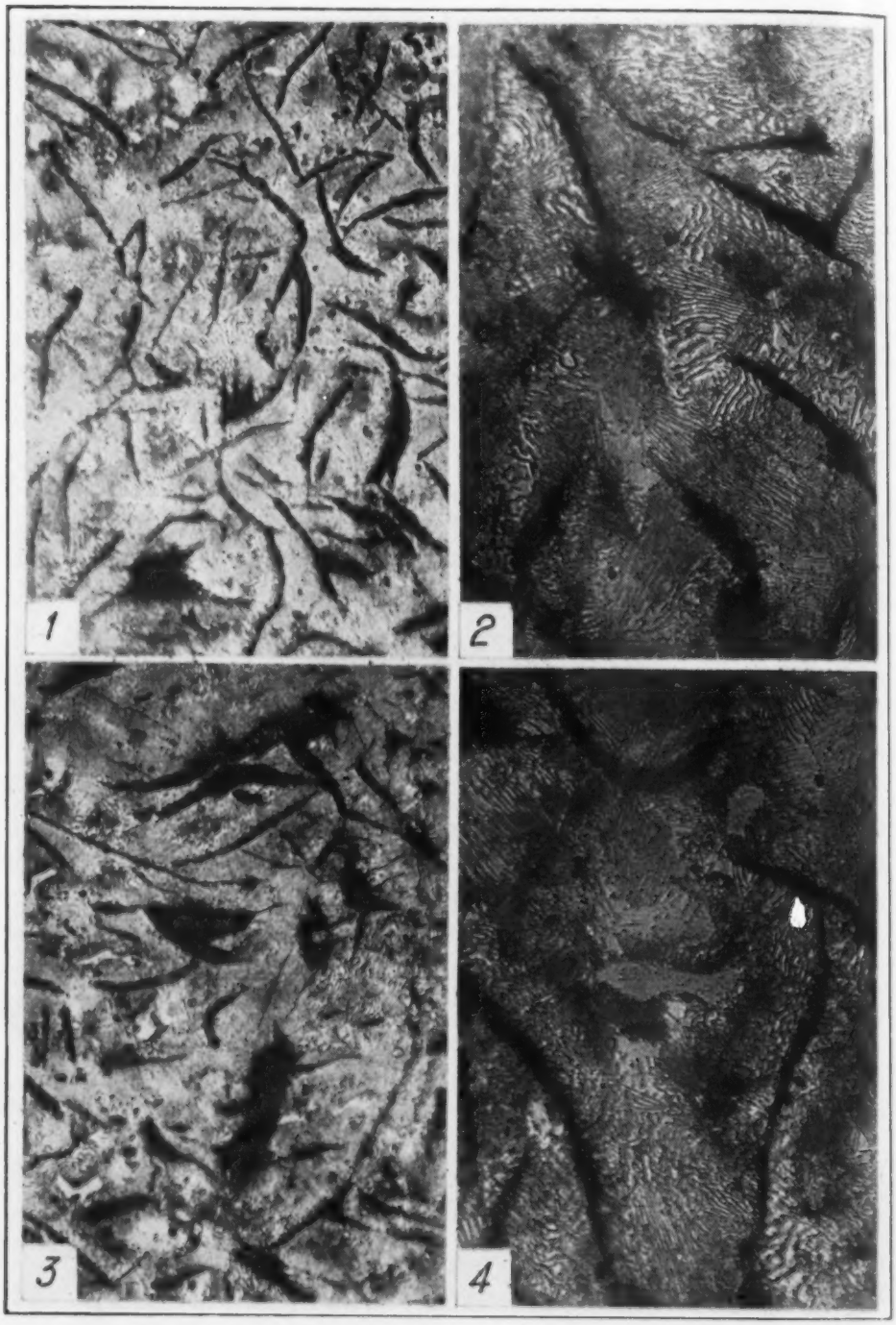


Fig. 1—Mixture No. 1 Showing a Spattering of Free Carbide in a Normal Fine-Grained Matrix. Superior to Regular Iron with Respect to Freedom from Ferrite. × 150.
Fig. 2—Same as Fig 1. × 500.
Fig. 3—Mixture No. 2 Similar to Mixture No. 1. × 150. Fig. 4—Same as Fig. 3. × 500.

a pearlitic matrix just entering into the sorbitic stage in places, with a uniform distribution of small carbide particles in a field of close-grained graphite. The addition of chromium in Mixture No. 3 has hardened the matrix somewhat by moving more of it from the pearlitic into the sorbitic stage and also has increased the size of the carbide particles. However, the latter effect is no further advanced than that which is encountered in the regular iron while the hardness of the nickel-chromium iron is 40 to 60 Brinell hardness number units greater.

The regular iron (No. 5) is largely pearlitic. It is studded with small particles of carbide which in respect to size would be classed somewhere between irons No. 3 and No. 4. It differs from the special irons in the fact that its matrix is expelling free ferrite, undoubtedly on account of the higher silicon content, and also tending to concentrate the carbide particles into knots which develop into "hard spots." The presence of free ferrite and also free carbides indicates that this is an unsafe structure, inclined toward segregation and a breaking down under heat into soft spots or hard spots with a resultant lack of uniform hardness.

This experiment indicates that much improvement in the Brinell hardness and structure of cast iron can be made with the addition of nickel and chromium starting at a point above 0.25 per cent chromium and maintaining the nickel-chromium ratio at approximately 3 to 1.

With each increase of 0.10 per cent above 0.25 per cent chromium the Brinell hardness number will increase approximately 10 points in a given section of this type base iron.

Effect of Chromium and Nickel on the Physical Strength Hardness and Structure of Iron for Large Tractor Cylinders

From the experience gained in the first investigation, several large tractor cylinders (cast separately) and the usual test bars were poured from a ladle to which had been added sufficient chromium and nickel to give a theoretical analysis of 0.35 per cent chromium and 1.00 per cent nickel. These were compared with several other cylinders cast on the same day from the same base mixture of iron, but, however, from a different ladle. Sections were cut longitudinally through the bore and Brinell readings taken at four points equally

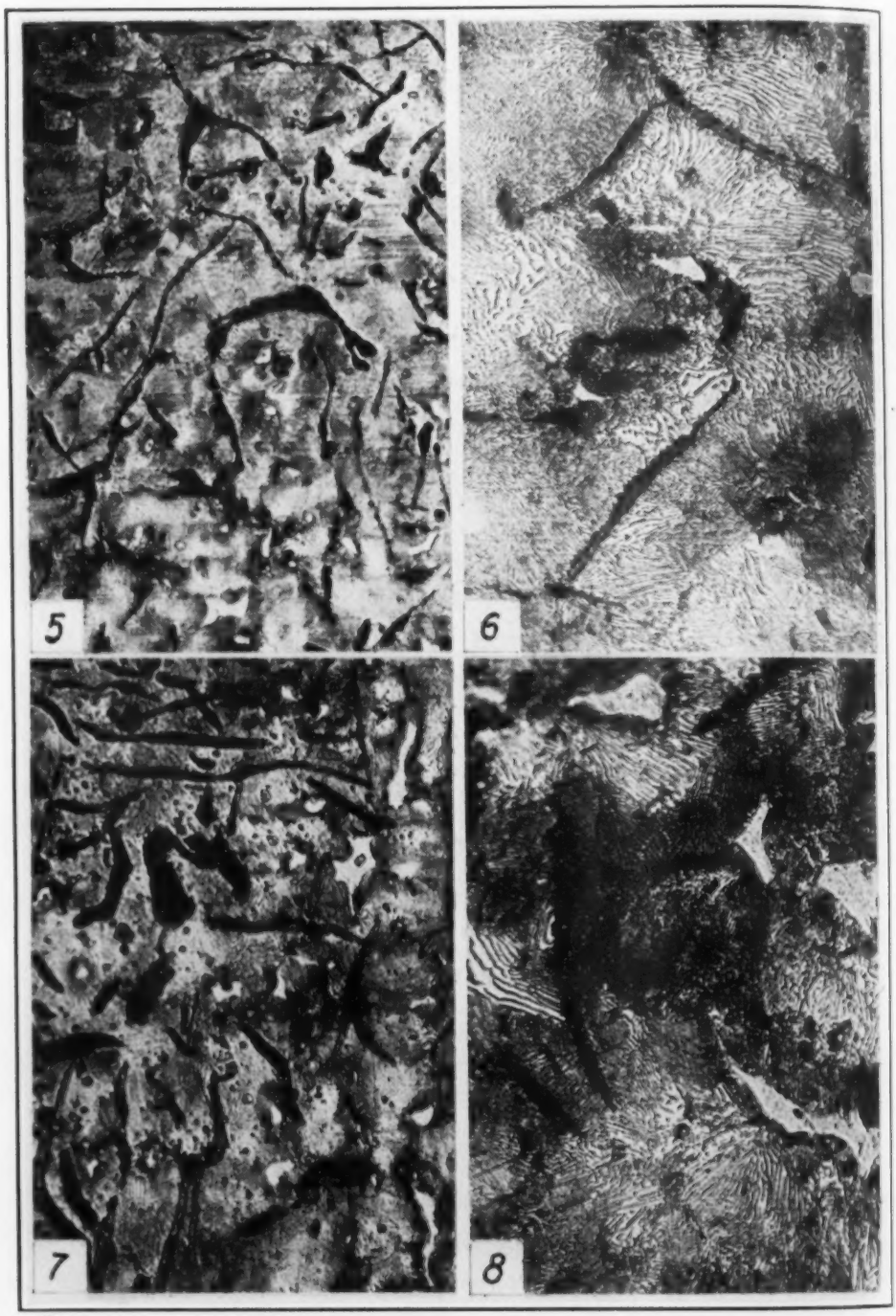


Fig. 5—Mixture No. 3 Showing Flatter and More Velvety Tone of the Matrix. Carbides more Numerous than Mixture No. 1 or 2. × 150. Fig. 6—Same as Fig. 5. × 500.
Fig. 7—Mixture No. 4. An Increase in Sorbitic Areas as Well as Free Carbides Accounts for Increased Hardness. × 150. Fig. 8—Same as Fig. 7. × 500.

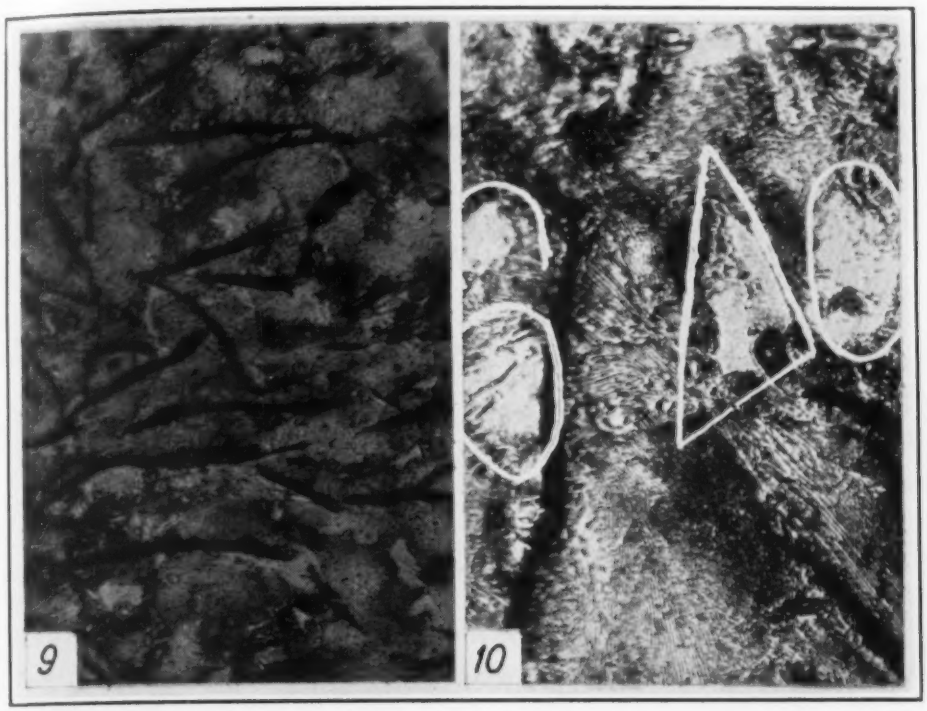


Fig. 9—Mixture No. 5. Similar to Fig. 1 but Contains More Free Ferrite which is Due to Higher Silicon Content. × 150. Fig. 10—Same as Fig. 9. × 500. The Circles Enclose Free Ferrite Areas while the Triangle Encloses Free Carbide Area.

spaced along the full length of the bore. The following tabulation shows this comparison as well as the analysis of the cylinders selected.

	Cylinder No. 1	Cylinder No. 2	Cylinder No. 3
Total Carbon	3.49	3.37	3.38
Combined Carbon*	0.70	0.57	0.49
Manganese	0.65	0.61	0.62
Phosphorus	0.157	0.158	0.152
Sulphur	0.109	0.138	0.141
Silicon	2.11	1.96	1.93
Nickel	1.10	0.29	0.30
Chromium	0.38	0.03	0.03
Brinell Hardness Number	217	170	187
	196	163	156
	207	156	170
	207	179	185
Average	207	167	174

*Sample for combined carbon taken midway between head contact face and lower junction of water jacket and bore.

It is readily noted that considerable increase in Brinell hardness number has been obtained through the use of 0.38 per cent chromium and 1.10 per cent nickel. This is the identical mixture which the previous investigation indicated would prove ideal for cylinder work. The following tabulation gives a comparison of the physical values

between the base iron and the iron from which the experimental cylinders were poured. Deflection and transverse tests were made on the bars "as cast" on supports 18 inches apart. A tensile test specimen (A.S.T.M. for cast iron) was made from one-half of each bar after the transverse tests were completed.

	Deflection in Inches			Transverse	Tensile Pounds
	1000 Pounds	2000 Pounds	Break	Stress	Per Square Inch
Base Iron	0.064	0.185	0.268	2457	34,600
Alloyed Iron	0.074	0.190	0.290	2665	35,975

A comparison of the structures of these two irons may be seen in Figs. 11 to 14 inclusive.

It is noteworthy that the alloy in this case has materially increased the Brinell hardness number of the cylinder as well as the transverse and tensile strength and this has been done in spite of the fact that the total carbon was 0.12 per cent higher and the silicon 0.15 per cent higher.

Discussion of Results

From the data of these two similar investigations we learn that it is possible to produce practically any desired hardness and structural improvement by properly adjusting the base mixture, depending on the metal thickness to be cast, then adding sufficient chromium to raise the Brinell hardness, and enough nickel to offset the excessive chilling effect which would result from additions of chromium alone.

Nickel alone added to any given base iron of the automotive type which is already suitable for a particular casting will not materially improve the casting except in machining qualities. In other words, either the silicon must be lowered to a point which would be dangerous and nickel added to offset the chilling effect of the low silicon, or chromium must be added and nickel introduced in an approximate ratio of 3 nickel to 1 chromium to offset the difficulties in machining with the addition of chromium alone.

The latter method is the most practical of application in the average production foundry due to the possibilities of producing many different grades of iron from one base.

We must not lose sight of the fact, however, that whatever alloys are used, the base mixture must be as high in quality as is possible to obtain and further improvement made by additions of al-

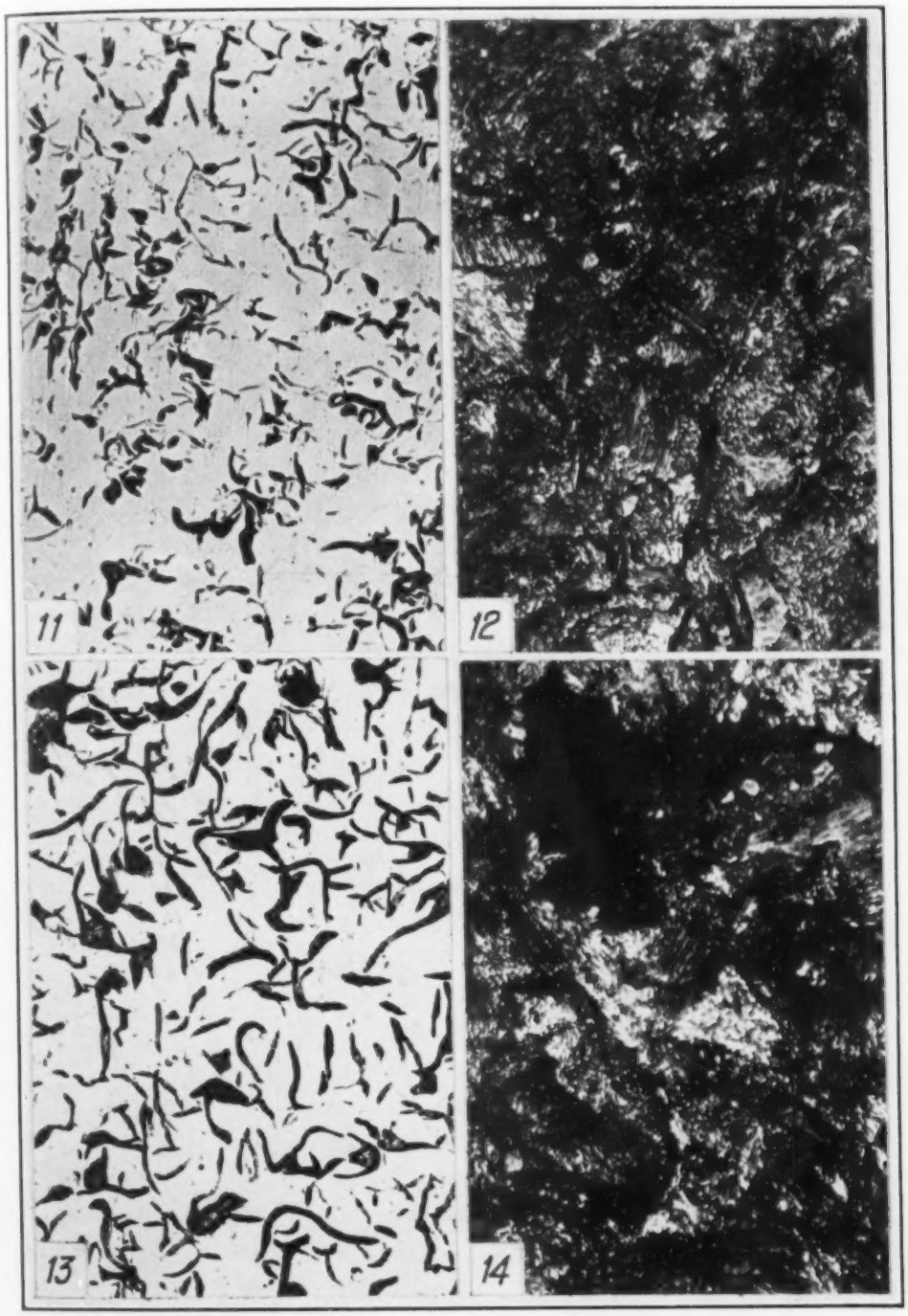


Fig. 11—Base Iron Cylinder No. 3 Showing Finely Divided Graphite. Unetched. × 100. Fig. 12—Same as Fig. 11 Etched. × 500.

Fig. 13—Alloy Iron of Cylinders No. 1. Graphite Coarser than Fig. 11 Due to Higher Total Carbon. Unetched. × 100. Fig. 14—Same as Fig. 13. Etched × 500.

loys. Alloys added to a poor or inferior grade of iron are only wasted.

Effect of Prolonged Heating on the Structure, Combined Carbon and Hardness of Several Cast Irons

The demand for increased speed and higher engine temperatures has created one more problem for the producers; that is, to make an iron which will not decrease in hardness when subjected to high temperatures for long periods of time.

In order to determine which type of iron might be the best suited under these conditions, six representative types were selected for investigation; three were plain iron and three others were made by the addition of nickel and chromium to the ladle from the same heats as the plain iron. Table II gives the analyses and physical properties of the six irons under investigation, as cast.

The specimens selected for the subsequent heat treatment were 1¼ inches in diameter and ¾ inches thick cut from the arbitration bars as cast. One set of specimens from each iron was heated in the electric furnace for 90 hours at a temperature of 600, 800, 1000, 1200, and 1300 degrees Fahr. Brinell hardness determinations were made after the first hour of heating, after which the specimens were returned to the furnace to complete the full 90-hour drawing period. Upon conclusion of the 90-hour heating, both Brinell hardness num-

Table II

		Analysis					Transverse 1¼-12 Inch			
Mix.	Type of Iron	Total Carbon	Combined Carbon	Silicon	Nickel	Chromium	Stress	Deflection	B. H. N.	Tensile Strength Pounds Per Square Inch
1	Plain Low Silicon	3.12	1.09	1.08	...	...	4030	0.125″	241	29,050
2	Mixture No. 1 plus Nickel and Chromium	3.10	1.05	1.13	1.21	0.39	4130	0.107″	286	31,550
3	Plain Medium Silicon	3.10	0.79	1.69	...	...	4160	0.138″	228	34,400
4	Mixture No. 3 plus Nickel and Chromium	3.15	0.90	1.76	1.13	0.45	5030	0.159″	262	44,450
5	Plain High Silicon	3.33	0.67	2.34	...	...	3420	0.129″	183	29,640
6	Mixture No. 5 plus Nickel and Chromium	3.35	0.82	2.32	0.86	0.41	3715	0.123″	217	34,580

Table III

Mixture	Type of Iron	Combined Carbon after drawing at different temperatures Degrees Fahr. As Cast	600	800	1000	1200	1300
1	Plain Low Silicon	1.09	1.14	1.20	1.22	0.09	0.05
2	No. 1 plus Nickel and Chromium	1.05	1.17	1.09	1.13	0.86	0.70
3	Plain Medium Silicon	0.79	0.90	0.87	0.48	0.05	0.03
4	No. 1 plus Nickel and Chromium	0.90	1.03	0.97	0.98	0.34	0.25
5	Plain High Silicon	0.67	0.65	0.59	0.42	0.05	0.02
6	No. 5 plus Nickel and Chromium	0.82	0.79	0.76	0.72	0.28	0.20

ber and combined carbon determinations were made on each set. The combined carbon determinations were secured in duplicate on all the specimens. The average results are given in Table III.

The combined carbon of the low silicon-nickel-chromium iron shows considerable stability when this iron is heated for long periods up to temperatures as high as 1300 degrees Fahr. while that of the higher silicon alloy irons held up better than any of the three plain irons. Of the three regular irons the low silicon is much the better having retained its combined carbon up to 1000 degrees Fahr. at which point the higher silicon types have lost nearly half of their combined carbon. Therefore, it appears that at temperatures below the critical of plain iron, the stability of the combined carbon is a function of the silicon content.

Probably the most striking feature concerning this series of irons is that the combined carbon of each iron remained at a fairly high level at 1000 degrees Fahr. and that it required the 1200 degrees Fahr. 90-hour draw to lower it to any serious extent. Still another very interesting point is the general increase of combined carbon of the two lower silicon irons with the drawing temperatures up to 800 degrees Fahr. and in some cases up to 1000 degrees Fahr. No satisfactory explanation can be given for this peculiar trend of the combined carbon in the comparatively lower temperature ranges. However, from 1000 to 1300 degrees Fahr. the 90-hour draws have an effect upon the combined carbons which in a marked degree favors the alloyed irons. Table IV lists the Brinell hardness number determinations made on the same specimens.

The Brinell hardness number determinations in general agree with the combined carbon shown at the same temperatures, except that no increase is noted as was the case in Table III.

In order to prevent so much repetition, only two of the six irons were studied microscopically. Those selected were the plain low sil-

Table IV

Mixture	Type of Iron	Brinell Hardness Number After 90 Hours of Heating Degrees Fahr.					
		As Cast	600	800	1000	1200	1300
1	Plain Low Silicon	241	223	223	228	107	109
2	No. 1 plus Nickel-Chromium	286	260	262	255	179	174
3	Plain Medium Silicon	228	228	223	203	112	110
4	No. 3 Plus Nickel-Chromium	262	262	262	255	135	140
5	Plain High Silicon	183	183	173	160	114	108
6	No. 5 Plus Nickel-Chromium	217	217	212	194	147	140

icon, and the medium silicon-nickel-chromium iron. It was felt that these two should prove the advantages or disadvantages of the alloyed irons with the plain iron placed in the most favorable position due to its low silicon content. It is evident from the analyses shown that photomicrographs of the others would not have had any specially distinctive structures other than those which are shown. Photomicrographs were made of these two irons after each of the following treatments. 1. As cast, 2. Drawn at 800 degrees Fahr.—90 hours, 3. Drawn at 1300 degrees Fahr.—90 hours. These are shown in Figs. 15 to 20 inclusive.

The matrix of the plain low silicon iron (Mixture No. 1) in the "as cast" condition (Figs. 15 and 16) is found to consist mainly of pearlite with little, if any, free carbide. The medium silicon-nickel-chromium iron (Mixture No. 4) has a pearlite sorbitic matrix containing a few free carbides but no free ferrite. Figs. 17 and 18 show the structure of these two irons after drawing for 90 hours at 800 degrees Fahr. It is evident that there has been little or no change produced with this treatment.

Drawing the irons at 1300 degrees Fahr. for 90 hours produces the structures shown in Figs. 19 and 20. It is seen that the matrix of the plain low silicon iron (Mixture No. 1) consists of nearly all free ferrite with only remnants of pearlite clinging to the large graphite flakes. This same treatment on the medium silicon-nickel-chromium iron (Mixture No. 4) produces a matrix which although largely ferritic still shows an appreciable percentage of pearlite scattered throughout.

An outstanding feature of this data is the confirmation of the fact that silicon is the most important element to be considered in heat resistant irons and that in each case the alloy iron was superior to the plain iron of the same, or even lower, silicon content.

Perhaps the most important relation between high Brinell hard-

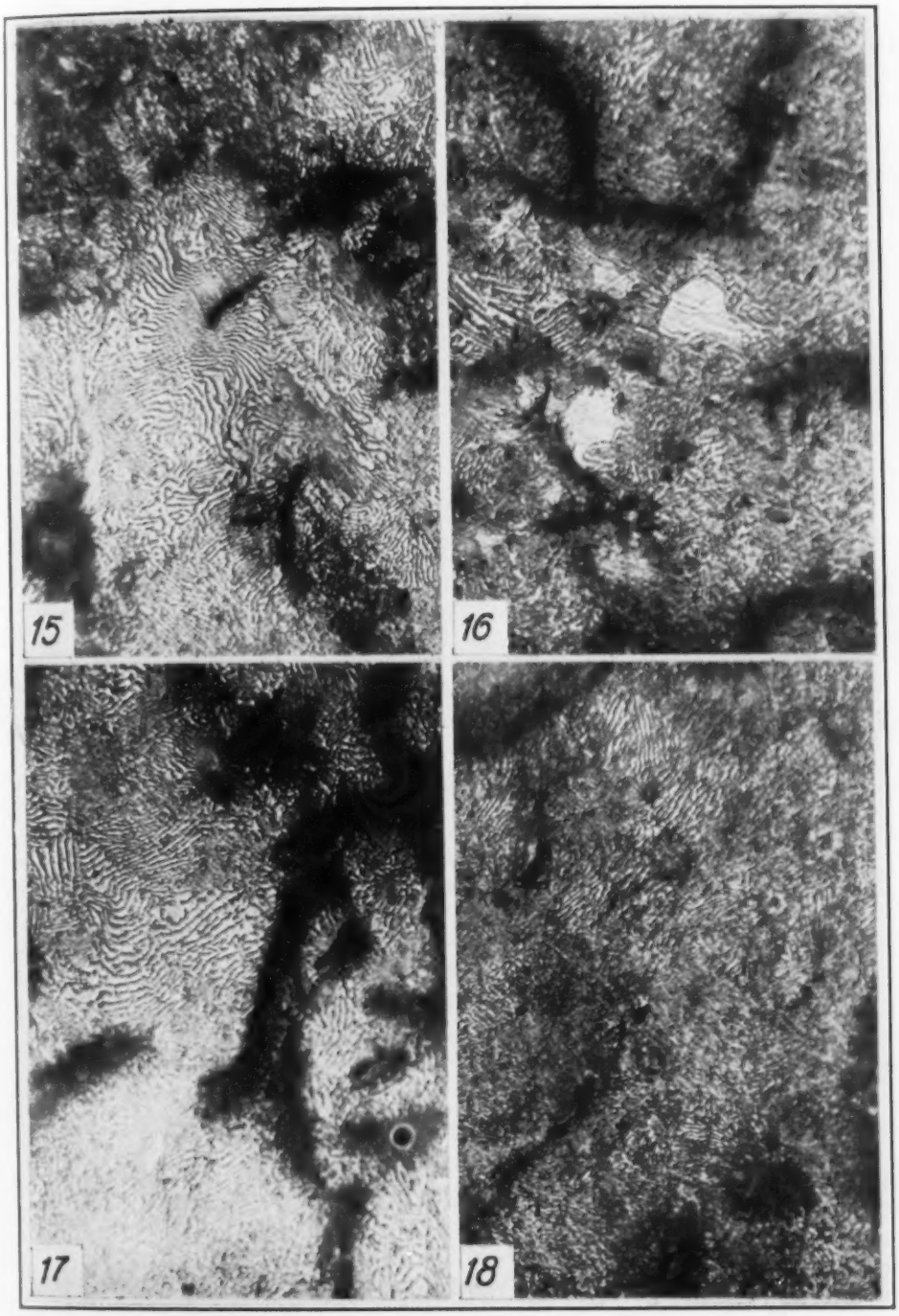


Fig. 15—Plain Low Silicon Cast Iron. As-cast. × 500. Fig. 16—Medium Silicon-Nickel-Chromium Iron. As-cast. × 500.
Fig. 17—Plain Low Silicon Iron Drawn at 800 degrees Fahr. × 500. Fig. 18—Medium Silicon-Nickel-Chromium Iron Drawn at 800 degrees Fahr. × 500.

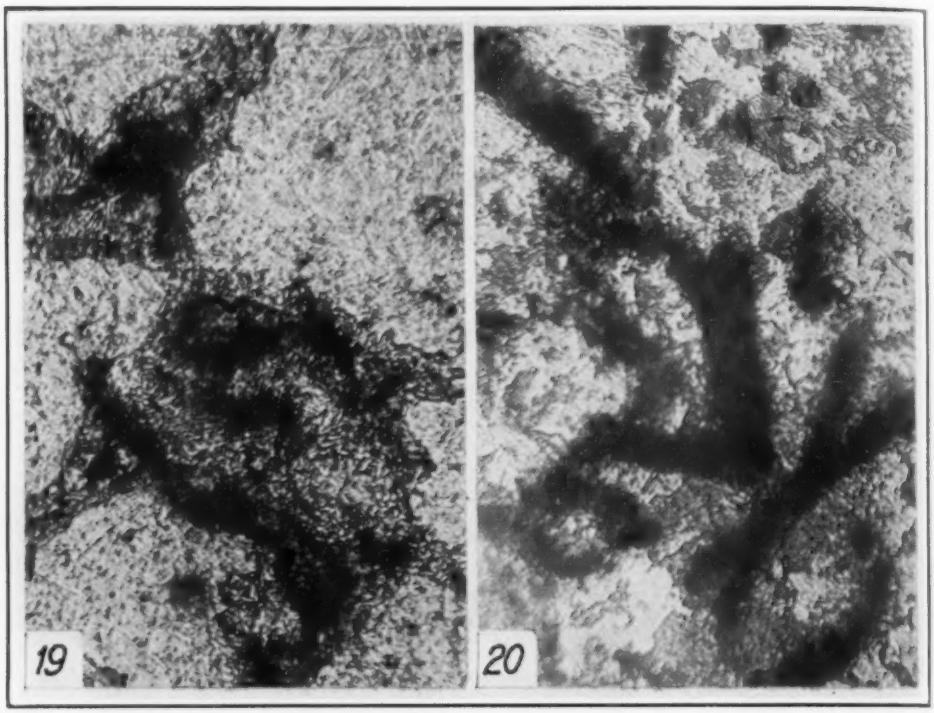


Fig. 19—Plain Low Silicon Iron Drawn at 1300 degrees Fahr. × 500. Fig. 20—Medium Silicon-Nickel-Chromium Iron Drawn at 1300 degrees Fahr. × 500.

ness number and heat resistant properties exists in the application of Diesel engine liners, brake drums, engine cylinders, heads, etc.

High hardness, if secured by producing a fine pearlitic-sorbitic matrix, is considered to be indicative of good wear-resistance. However, if the high hardness is produced by free carbides, good wear-resistance does not necessarily follow and the carbides may actually be harmful, as in the case of brake drums, where it is thought that free carbides tend to tear the brake lining. If, in conjunction with a high pearlitic sorbitic hardness, the iron possesses good heat resistant properties, it is then an ideal material for the applications mentioned.

Production of Chilled Roller Castings Through the Use of Ferrochromium

Rollers or idlers as they might be called support the moving track of the track-laying type tractors. They are subjected to excessive wear and it is therefore necessary that the depth of chill on the face of the casting be maintained within narrow limits. These castings are poured in a permanent mold and experience has proved

that there is a definite relation between the chill depth on a test piece poured against a chill and that which is produced in the casting poured from the same ladle. For this reason a chill test piece is made from each ladle poured into such castings and the castings are either accepted or rejected on the depth of chill obtained from the chill test.

Formerly it was the practice to make special cupola charges for these castings by lowering the silicon content and increasing the percentage of steel. Since there are several different sizes of rollers varying from 25 to 125 pounds, each requiring the same chill depth on the tread, it was necessary to make special mixtures for each size to compensate for the difference in weight and section of the castings. These special charges were either introduced at the beginning of the heat or at such a time that they would melt down during the lunch hour and so be poured while the remainder of the foundry was shut down. Since the tonnage of these castings is small and accurate control difficult to obtain, this method was a source of much inconvenience in an otherwise continuous cycle of melting.

It was only natural, therefore, that we should attempt to find some method by which we could alloy the regular grade of iron in the ladle and pour these special castings at any time during the day. Since chromium is a powerful agent against graphitization, it was selected as the alloy to be used.

The test procedure was as follows: From a mixing ladle (3 tons) of regular iron a set of arbitration bars, and a chill test specimen were poured and designated as "A." To a ton of iron from this same ladle 15 pounds of 70 per cent ferrochromium was added and a similar set of castings poured and designated as "B." To still another ton of iron from the same large ladle 25 pounds of ferrochromium was added and another set of castings poured and marked "C."

Analyses of millings taken from the fractured ends of the transverse bars are given in Table V.

Table VI gives a comparison of the physical values obtained from the test bars poured from these different grades of iron.

The chill depth and hardness of chill as determined on the standard chill test specimens are shown in Figs. 21, 22 and 23. Rockwell "C" readings $\frac{1}{16}$-inch apart were taken in the center of the cross section shown after polishing.

Hardness tests were made on a section through the hub and

Table V

Iron	Total Carbon	Combined Carbon	Silicon	Per Cent Manganese	Phosphorus	Sulphur	Chromium	Nickel
A	3.43	0.65	2.04	0.63	0.160	0.120	0.05	0.18
B	3.40	0.79	2.02	0.62	0.163	0.125	0.51	0.19
C	3.44	0.91	2.00	0.61	0.159	0.121	0.87	0.20

tread of a typical roller poured with chromium-treated iron. The average hardness on the hub ends before machining was 217 compared to 179 for rollers taken from regular production which had been made from the special cupola charges. As the results of this test proved very favorable, this method of producing these grades of iron was adopted and has been in regular use for some time.

Table VI

	Transverse—Standard Bar 18-inch Centers				
	Deflection—Inches			Transverse	Tensile Pounds
Irons	1000 Pounds	2000 Pounds	Break	Stress-Pounds	Per Square Inch
A	0.064	0.185	0.268	2450	34,600
B	0.057	0.152	0.234	2600	40,200
C	0.049	0.129	0.216	2625	41,450

In addition to producing a chilled casting of superior quality it lends itself to simple control as in regular production the amount of ferrochromium added in the alloying process is varied inversely as the depth of chill which is obtained from the regular iron at that particular time.

Table VII gives a comparison of values obtained from a number of test bars poured over a period of approximately six months, during regular production by the old and the new method for grade No. 1.

Table VIII gives a similar comparison for No. 2 grade.

This particular experiment affords a good opportunity for studying the effects on combined carbon and physical values which may be obtained by the addition of ferrochromium to cast iron of medium silicon content. The increase in combined carbon has been marked and almost directly proportional to the amount of chromium added, while at the same time a corresponding decrease in deflection is noted. This is in direct contrast to the action of nickel.

It is also of interest to note that chromium-alloyed iron produces greater hardness at the face of the chill which is indicative of

Table VII

No. 1 Grade
(30% Pig—47½% Scrap—22½% Steel)

	T.C.	C.C.	Si.	Cr.	Ni.	Chill Depth	Deflection 1000	Deflection 2000	Deflection Break	Transverse Stress	Tensile lbs./sq. in.
	3.14	.72	1.92	.06	.12	7/16"	.055"	.157"	.230"	2425	35,900
	3.47	.86	1.82	.13	.11	3/8"	.069"	.167"	.229"	2400	37,400
	3.42	.77	1.81	.06	.08	1/2"	.065"	.165"	.239"	2450	37,475
	3.43	.71	1.89	.09	.08	5/16"	.072"	.204"	.246"	2275	34,750
	3.25	.69	1.80	.14	.14	7/16"	.060"	.160"	.218"	2310	35,600
Avg.	3.37	.75	1.85	.10	.10	13/32"	.064"	.171"	.232"	2372	36,225

BASE IRON
(35% Pig—52½% Scrap—12½% Steel)
(Plus Ferrochromium)

	3.40	.76	1.96	.47	.14	3/8"	.061"	.162"	.249"	2560	37,700
	3.35	.79	2.04	.36	.19	3/8"	.060"	.160"	.241"	2525	38,200
	3.46	.90	1.90	.44	.34	7/16"	.050"	.136"	.221"	2650	41,700
	3.49	.74	2.01	.56	.17	3/8"	.047"	.141"	.221"	2640	42,000
	3.43	.74	2.11	.61	.30	3/8"	.040"	.125"	.215"	2735	43,100
	3.46	.74	1.95	.51	.10	3/8"	.065"	.169"	.252"	2535	39,000
	3.46	.83	2.02	.59	.13	3/8"	.064"	.157"	.242"	2610	42,500
	3.40	.71	1.95	.35	.28	5/16"	.061"	.146"	.240"	2700	43,000
Avg.	3.43	.78	1.99	.48	.21	3/8"	.056"	.150"	.235"	2620	40,900

Table VIII

No. 2 Grade
(10% Mayari—20% Other Pig—35% Scrap—35% Steel)

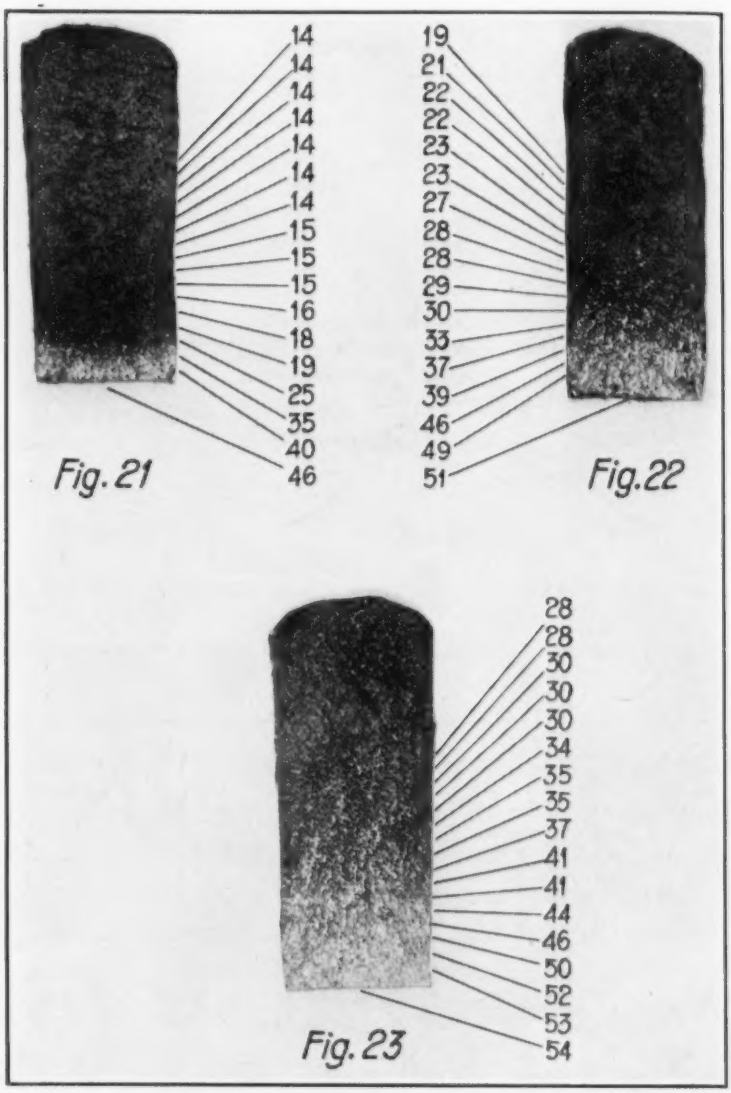
	T.C.	C.C.	Si.	Cr.	Ni.	Chill Depth	Deflection 1000	Deflection 2000	Deflection Break	Transverse Stress	Tensile lbs./sq. in.
	3.24	.82	1.85	.13	.12	7/16"	.601"	.166"	.240"	2425	38,300
	3.26	.79	1.83	.13	.10	5/8"	.057"	.158"	.210"	2350	36,500
	3.49	.82	1.74	.12	.11	9/16"	.062"	.155"	.222"	2300	38,500
	3.34	.71	1.48	.15	.10	3/4"	.064"	.162"	.235"	2560	39,725
	3.43	.79	1.66	.17	.13	11/16"	.062"	.160"	.226"	2360	37,600
Avg.	3.35	.78	1.71	.14	.11	5/8"	.061"	.160"	.226"	2400	38,125

BASE IRON
(35% Pig—52½% Scrap—12½% Steel)
(Plus Ferrochromium)

	3.50	1.01	1.82	.90	.12	11/16"	.051"	.313"	.191"	2540	39,200
	3.41	.74	1.91	.74	.50	3/4"	.050"	.120"	.252"	2625	43,700
	3.55	.87	2.01	.88	.11	9/16"	.050"	.141"	.221"	2660	42,900
	3.52	1.03	2.17	.95	.21	5/8"	.045"	.124"	.200"	2640	41,400
Avg.	3.49	.91	1.98	.87	.24	5/8"	.049"	.129"	.216"	2616	41,800

greater wearing qualities, and in addition greater hardness is shown in the gray section behind the chill while there is no sudden break in hardness at this point, as there was with iron showing the same chill depth made by the old method.

The general averages prove the chromium-treated iron to be approximately 6000 pounds per square inch stronger than the regular cast iron and even 4000 pounds per square inch stronger than a lower silicon iron of higher steel content.



Figs. 21, 22 and 23—Showing the Results of Hardness Tests Made on Standard Chill Test Specimens. Rockwell C. Readings $\frac{1}{16}$ inch Apart were Taken in the Center of the Cross-Section After Polishing. Fig. 21—Iron "A" Chill Depth $\frac{1}{8}$ Inch. Fig. 22—Iron "B" Chill Depth $\frac{5}{16}$ Inch. Fig. 23—Iron "C" Chill Depth $\frac{9}{16}$-Inch.

General Summary

Chromium in iron increases the hardness, strength, etc. by combining the carbon and producing a more stable double carbide of iron which crystallizes out with the pearlite, while nickel tends to dissolve this free cementite, forming pearlite. A combination of the two alloys in the ratio of approximately 3 nickel to 1 chromium will

produce an iron for automotive type cylinders which is superior to plain iron with respect to hardness, strength and microscopic structure. The percentage increase of these properties varies as the per cent of alloys uesd.

Increased Brinell hardness if accompanied by excessive free cementite is not desirable, but when produced by a pearlitic or pearlitic-sorbitic structure it is an indication of increased quality.

Nickel-chromium alloyed irons are much superior with respect to heat resistant properties than ordinary irons.

Irons alloyed with chromium produce a superior chill and afford a practical method for production of special castings of this type.

Acknowledgment

The author wishes to acknowledge the assistance given by M. J. Gregory, factory manager, foundry division, Caterpillar Tractor Co.; and G. C. Riegel, chief metallurgist, Caterpillar Tractor Co., for taking part of the photomicrographs.

DISCUSSION

Written Discussion: By V. A. Crosby, foundry metallurgist, Studebaker Corp., South Bend, Ind.

Mr. Shipley's paper has been well written and covers the subject of chromium-nickel alloy cast iron very well. It is regretable that molybdenum and vanadium were not included since they are most assuredly alloying elements of considerable importance. Molybdenum with nickel has remarkable physical properties. The cost, however, is somewhat against it.

In the first paragraph, speaking of greater hardness, greater wearing properties and improved strength for automotive castings, I do not agree with the statement "these requirements had exhausted the ordinary resources of the production foundry," for the reason that the total carbon content mentioned under the heading "plain cylinder iron" is so high that it could hardly be labeled the last word in cupola practice. It has been our experience that total carbon percentages in excess of 3.30 per cent are unsatisfactory for automotive cylinders.

The use of chromium and nickel as an alloying agent in cast iron has been pretty well demonstrated and little argument can be offered against its use except from an economical standpoint. Whether it is worth the difference is the problem that is ever with us.

On page 142, we note that a 0.24 per cent reduction in silicon was made in these charges to which the alloy was added. These results could hardly be classified as comparable.

Our experience indicates that a great improvement in structure can be made in automotive cylinder iron by lowering the total carbon to 3.00 or 3.10

per cent. The writer would not advise going any lower because of cracks showing up in the castings. We have no trouble securing 190-202 Brinell in cylinder block bores using a plain cylinder iron with 3.10 per cent carbon and 1.90 per cent silicon. This same iron with 0.25 per cent chromium addition gave 228 in the bore with, of course, increased difficulties in machining.

We agree with the author that there is an increase of 10 points Brinell for each 10 points of chromium addition, and that there must be twice to three times as much nickel used as chromium to break down the stable double carbides of iron and chromium. The photomicrographs show that many chromium-iron carbides exist even with the addition of nickel. The breaking down into pearlite and ferrite is in direct relation to the temperature of the molten iron, per cent of nickel and the content of chromium added. Hot iron is necessary with any alloy addition, but especially so with chromium additions.

The author's statements at the bottom of page 148 and at the top of page 150 are well taken and in line with the generally accepted attitude toward the use of alloys for producing better gray iron.

The writer is of the opinion that chromium either alone or in combination with other elements should not be added to motor block iron because of the ever present double carbides of iron and chromium which may or may not be broken down into pearlite and ferrite.

Some very remarkable results are being obtained by the use of nickel and molybdenum in the ratio of 1:1. These results are obtained by strengthening the metallic matrix of the metal and results are not dependent upon dispersion of the hard stable carbides of chromium.

Written Discussion: By W. J. Diederichs, metallurgist, The Autocar Co., Ardmore, Pa.

The author is to be congratulated for a clear demonstration of the improvement to be made by the alloying of cast irons and for a restatement of these gains and the proper procedure to be used in their attainment. Of particular significance are the statements in his discussion on page 148. These statements appear to us to be a clear-cut concise summary of the proper considerations to be borne in mind.

The author presents data (page 156) which clearly indicate that chromium increases hardness and strength sharply and reduces deflection below that of the plain base iron. He points out that it increases chill. It necessarily, therefore, increases nonuniformity of properties in an intricate casting. Data (page 148) showing the effect of adding nickel to a chromium bearing iron of a similar base material indicate that the further addition of nickel increases the deflection beyond that of the plain base iron and it reduces chill and the nonuniformity of properties throughout an intricate casting.

These results are important in a casting such as a cylinder block subject to differential chilling as cast and to differential heating and therefore stressing in service.

The nickel-bearing irons show an advantage against subsequent warping and cracking in such service and, as the author demonstrates, they hold their hardness better under heat in service.

For its possible value as an addition to the author's data, we are giving

here the analysis which experience has indicated to us is excellent for cylinder blocks. These blocks are annealed at 900 to 950 degrees Fahr. to relieve casting stresses and minimize warpage in service. Hardness is held to limits 190-225 Brinell and the blocks offer no undue machining difficulties.

Constituent	Specified Per Cent	Usual Per Cent
Total Carbon	3.4 Max.	3.2 -3.35
Manganese	0.50-0.70	0.60-0.65
Silicon	Open	2.1 -2.25
Phosphorus	0.20 Max.	0.14-0.16
Sulphur	0.12 Max.	0.09-0.12
Chromium	0.35-0.60	0.45-0.55
Nickel	1.25 Min.	1.30-1.45

The transverse test of this material will consistently show 3800 to 3900 pounds and 0.11-0.12 inches deflection on 1¼-inch bars on 12-inch centers.

The part of the paper concerned with the effect of annealing various cast irons is very interesting but extremely puzzling. We would expect the microscope to show the presence of ample excess carbides in low silicon plain or alloyed irons, as mix #1, but Fig. 15 shows none and the author states that practically none is present. Still, he reports the combined carbon as 1.05 to 1.09 per cent and this is decidedly beyond eutectoid concentration.

After heating at low temperatures he reports an increase in combined carbon but no change in structure. Certainly combined carbon in such quantities should show up as excess carbides for the eutectoid ratio of cast irons is admittedly lower than 0.9 per cent carbon. We believe that full pearlitic matrix in cast irons is usually obtained when combined carbon runs between 0.6 and 0.8 per cent. We feel that the combined carbons reported do not agree with the structures shown and, further, unless cooling rate was retarded, the structures shown for the low silicon mixes and possibly the medium silicon mixes do not appear normal. As stated, we would expect to find excess carbides in the structure.

That combined carbon increases upon low temperature annealing of medium and low silicon irons is difficult to believe and will require further verification. We know of no other observations of a similar nature. Iron carbide, however, is not stable at temperatures below the critical and should break down to ferrite and graphite upon heating, as it evidently does in this case at temperatures above 1000 degrees Fahr. There is no obvious reason why it should act otherwise at lower temperatures if any change occurs at all. Since hardness in cast irons is in general directly proportional to the amount of combined carbon present, the author's Brinell data indicate that the combined carbon decreased rather than increased.

We are particularly interested in the change in Brinell hardness obtained upon annealing. These data indicate that any cast iron drops off sharply in hardness when heated for long periods above 1000 degrees Fahr. and in commercial mixes the drop starts at lower temperatures. The author does not report the hardness results obtained after one hour of heating but they no doubt follow the same general trend, possibly showing analogous reductions in

hardness at somewhat higher temperature. We would welcome a report of the results obtained.

The present trend in cast irons is to the high strength type of either the plain carbon or alloyed variety. Not infrequently, machining difficulties are encountered due to chill or hard spots (both due to excess carbides) and the difficulty is overcome by annealing. Temperatures in the red heat are required to eliminate hard spots and to correct the machining difficulty and these data indicate that the drop in hardness is excessive. The drop in hardness is due to breakdown of carbides and pearlite and is associated with a reduction in physical properties and wear-resistance. We question the advisability of ever annealing a casting to eliminate hard spots, even in alloyed irons where strength is better maintained, if strength is of importance in the application and feel that it is better practice to hold castings a little on the soft side so that annealing for machinability does not become necessary. We believe that annealing of cast irons should only be carried out for relief of casting stresses and then at temperatures preferably not higher than 900 to 1000 degrees Fahr.

Written Discussion: By H. H. Ashdown, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

This paper is of particular interest to makers of cylinders and cylinder blocks for internal combustion engines. There is no room for question of the marked advantages of the addition to cast iron of nickel and chromium in the proportions outlined by the author.

This alloy cast iron has unquestionably overcome many of the difficulties previously encountered under service conditions, the valve seat not only gives longer life by resisting deformation due to hammering but also one of the major difficulties, resistance to "pick-up" from the valve seat has been successfully overcome. Machining is more uniform and the cylinder walls present a smoother wearing surface and give longer life.

The writer would like to learn from the author if in his experience with this alloy he has noticed any marked difference in the general qualities of the cylinders by varying the casting temperature and at what temperature he has obtained the best and most consistent results.

The addition of calcium silicide to alloy cast iron shows, on physical properties, the same improved relative values as when added to straight grey iron and it would be of interest to learn if the author has found the properties to be further enhanced by this addition.

Written Discussion: By C. O. Burgess, Union Carbide and Carbon Research Laboratories, Long Island City, N. Y.

Mr. Shipley's able paper is timely in view of the wide interest in alloy cast iron. The fact that the foundryman must take advantage of the superior properties conferred on cast iron by certain alloy additions, in order to obtain greater wear-resistance, improved structure and resistance to high combustion temperatures, is brought out by the author. It is significant that the author has found that the addition of chromium is the most effective agent in the improvement of cylinder iron.

On page 142 of the paper he gives hardness figures on a series of cylinders cast from irons of varying alloy content. Cast iron No. 4 containing 0.37

per cent chromium and 0.49 per cent nickel is found to be ideal from a hardness standpoint but is criticized as showing variation in hardness through the length of the bore, although this variation is less than that shown by unalloyed iron. However, if the Brinell values on the cylinder cast from mixture No. 4 are examined, it will be noted that with the exception of the extreme readings taken at each end of the cylinder the variation along the bore is only 8 points Brinell hardness. That is, in the main section of the bore the evenness in hardness is equal or superior to that of cylinders cast from any other mix considered. The maximum hardness at the extreme ends of the cylinder made from this mixture No. 4 is only 26-32 Brinell points higher than the average bore hardness and exceeds the hardness of cylinder No. 1 (page 147), particularly recommended by the author, by only ten Brinell points. In this regard it is of interest to note, that cast iron hardened by chromium additions, up to at least the maximum hardness (227 Brinell) exhibited by this cylinder, does not show any serious loss in machining qualities. Mixture No. 4 also possesses the greatest strength of any of the cast irons of this series, the strength of the cast iron increasing with increase in chromium content.

It is again evident in this paper as in previous investigations that chromium is a most active agent in preventing deterioration and consequent wear of cylinders under the effect of heat or high combustion temperatures.

In view of Mr. Shipley's reported results and recent work by Th. Klingenstein in which he finds that chromium is all important when considering wear or heat resistance, it would seem evident that much greater stress should be placed on the chromium content of cast iron. Excellent results can evidently be obtained by the use of chromium, alone or in conjunction with small amounts of other alloying agents.

Author's Closure

We have not done enough work with vanadium to be able to discuss it freely. However, we have conducted a few experiments which might be rather interesting with respect to molybdenum.

Four alloy cast irons were made from the same ladle of base iron. These were molybdenum, chromium, nickel-molybdenum and nickel-chromium. The analysis and physical properties obtained from test bars of these irons are as follows.

Name	T. C.	C. C.	S.	Mn.	P.	S.	Cr.	Ni.	Mo.	Defl.	Tens.
Base Iron	3.30	.77	2.10	.62	.160	.160	.05	.34	...	.270	34450
Base Iron and Mo.	3.30	.81	2.10	.62	.160	.160	.05	.34	.31	.317	37900
Base Iron and Cr.	3.30	.76	2.10	.62	.160	.160	.44	.34	...	.300	37000
Base Iron and Ni-Mo.	3.30	.70	2.10	.62	.160	.160	.05	1.35	.37	.294	42450
Base Iron and Ni-Cr.	3.30	.80	2.10	.62	.160	.160	.46	1.14	...	.262	37350

In addition to the increase in physical properties which is indicated in the above table, photomicrographs show the strong tendency of molybdenum to break up graphite and distribute it uniformly over the field. In this respect we might add that the nickel-molybdenum iron was almost ideal in structure but of course the cost of an iron of this kind is nearly prohibitive.

I will agree with Mr. Crosby that iron containing over 3.30 per cent total

carbon is not as desirable as one below that figure. However, I still believe that irons containing 3.00 to 3.10 per cent total carbon can be still further improved by the use of alloys.

In view of the thousands of chromium-alloyed cylinder blocks which have proved their value on actual road tests, I believe Mr. Crosby has made a pretty strong statement when he says that "Chromium either alone or in combination with other elements should not be added to motor block iron."

In reply to Mr. Diederichs' question concerning the high combined carbon, I will say that the cooling rate in the low silicon irons was rapid enough to hold combined carbon slightly above the pearlitic concentration limit and thus the structure does not show excess free carbide. In other words it is not a true pearlitic structure but is slightly sorbitic. The solubility of combined carbon in low silicon irons is slightly higher than in high silicon irons.

In reference to Mr. Ashdown's discussion may I say that we have never done any work with varied casting temperatures since it is absolutely necessary to get the iron as hot as possible in order to dissolve the alloy and still maintain high enough temperature to pour an intricate casting. The temperature normally at the spout is 2800 degrees Fahr. or better before the alloy is added.

Neither has any work been done with the addition of calcium silicide to alloy cast iron.

In answer to Mr. Burgess' discussion it has been our experience with respect to cylinders that any addition of chromium which is not offset by additional silicon or nickel will cause considerable difficulty in machining at the usual production rates.

IDENTIFICATION OF INCLUSIONS IN STEELS

By Leland E. Grant

Abstract

Examination of inclusions at high magnification shows them to be nonhomogeneous in many cases. The various etching reagents used in the systematic examination of inclusions for their identification were applied to inclusions containing two or more phases. The results are shown in a series of photomicrographs. It is suggested that additional and more selective reagents are required before complete identification of the phases of complex inclusions can be established with certainty by etching tests.

IN connection with the examination of many failed parts from locomotives and cars, also from other sources, the author has had occasion to attempt to determine the nature of the inclusions found in the metal. The method of Campbell and Comstock[1], as modified by Wohrman[2], was used. It was found to be satisfactory only for making broad distinctions, as, for example, between oxides, sulphides, and silicates. While this perhaps is about all that is claimed for it there appears to be possible a refinement and elaboration of the general scheme which would make it satisfactory for finer distinctions. It is the purpose of this paper to point out some of the distinctions that appear desirable. It will also be shown that inclusions in commercial steels are not always the comparatively simple substance one might conclude them to be from the methods proposed for their identification and from microscopic examination of transverse specimens at low magnifications.

The matter of inclusions in steel has become increasingly important with the growth of the demand for clean steel, especially for critical forgings. Specifications including this feature are becoming increasingly common. Due to the lack of precise informa-

[1]Campbell and Comstock, "Method for the Identification of Non-Metallic Inclusions in Iron and Steel," *Proceedings*, American Society for Testing Materials, Vol. 1, 1923, p. 521.

[2]C. R. Wohrman, "Inclusions in Iron," Transactions, American Society for Steel Treating, Vol. XIV, 1928.

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, Leland E. Grant, is a member of the society and is chief chemist, Chicago, Milwaukee, St. Paul and Pacific Railroad Co., Milwaukee. Manuscript received June 18, 1931.

tion on the subject only general terms can as yet be used in such specifications. The total quantity and distribution of foreign particles are the chief concern of the consumer at present, although it probably is true that all inclusions differ to some extent in their harmful effects on the metal. But before it will be possible to determine the effect of various types of inclusions on steel, desirable as this is, a means of identifying the various types of inclusions must first be available. It is also apparent that inclusions cannot be expected to be simple substances. In any of the steel-making methods binary and ternary inclusions can be looked for since oxides of silicon, iron, and manganese are certain to be present as well as sulphides. Not only for identification is such a system desirable but it would also be of value to the steel maker in his efforts to eliminate inclusions as completely as possible.

It is assumed that the reader is somewhat familiar with the systematic method of identifying inclusions referred to above. For convenience, however, there is presented below a list of the reagents referred to in this paper and the time required for etching.

Reagent	Concentration	Time Applied
Nitric Acid	10 per cent in alcohol	10 seconds
Chromic Acid	10 per cent in water	5 minutes
Alkaline Sodium Picrate	25 grams Sodium Hydroxide 2 grams Picric Acid Water to make 100 c.c.	5 minutes (boiling)
Stannous Chloride	Saturated solution in alcohol	10 minutes
Hydrofluoric Acid	20 per cent in water	10 minutes

These were applied in the order given and it is understood that where a specimen is mentioned as having been etched in any of the reagents it had previously been etched in all those above it in the table. Sulphur printing was a separate test and was made on the specimen as polished. No further tests were made on such a specimen before repolishing.

Sulphide Inclusions

A typical sulphide inclusion before and after sulphur printing for 20 seconds with 2 per cent aqueous sulphuric acid is shown in Figs. 1 and 2. It will be noted that the inclusions were not a single substance, as small black particles can be seen adhering to the main masses of impurity. The inclusions were removed by sulphur print-

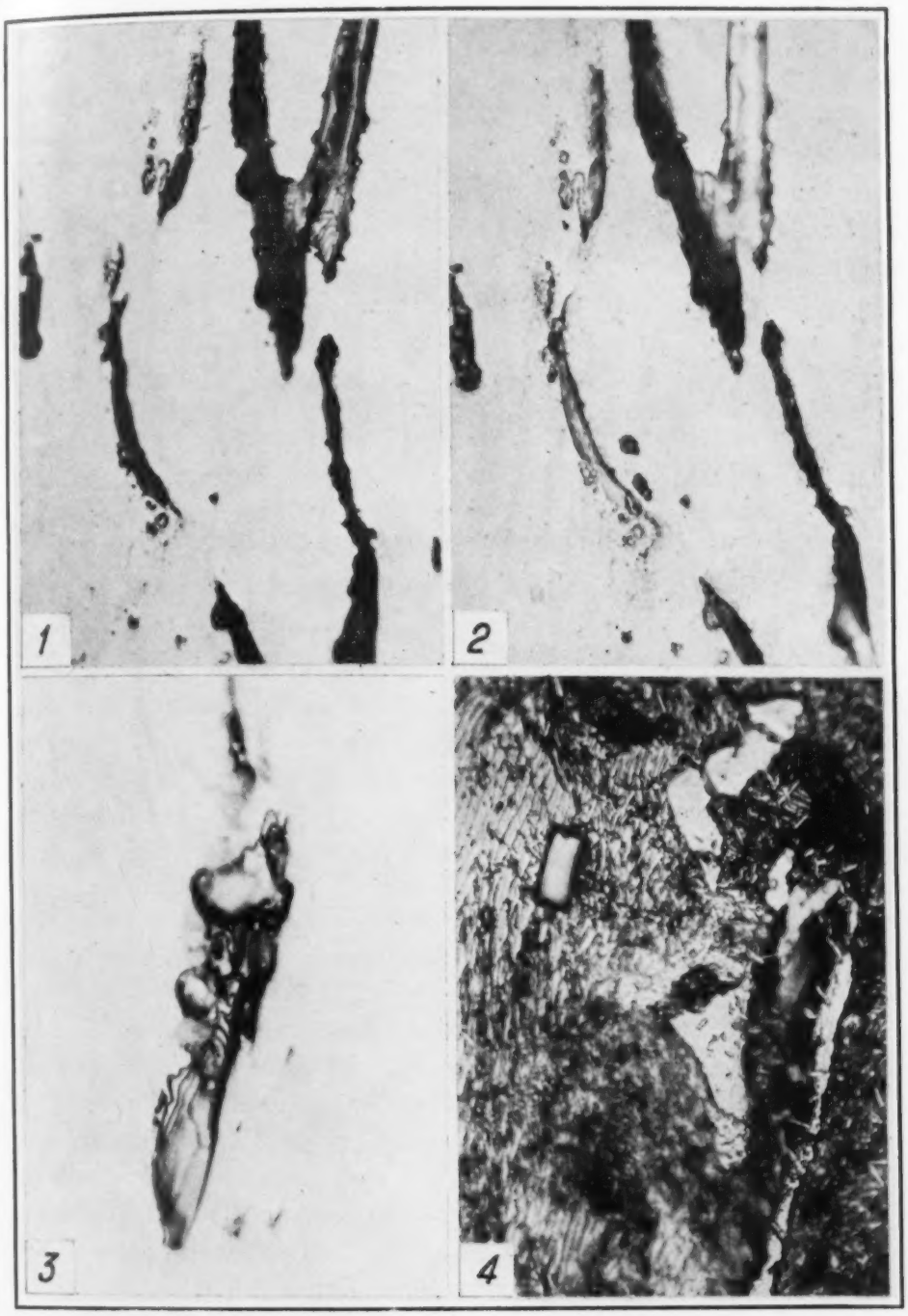


Fig. 1—Photomicrograph of a Sulphide Inclusion Unetched, × 1000.
Fig. 2—Photomicrograph of the Same Sulphide Inclusion Shown in Fig. 1 After Sulphur Printing, × 1000.
Fig. 3—Photomicrograph of the Eutectic Structure of a Sulphide Inclusion, × 1500.
Fig. 4—Photomicrograph of a Sulphide Inclusion After Etching in Chromic Acid, × 1000.

ing showing that they were sulphides. Fig. 3 shows clearly the laminated structure frequently seen in sulphide inclusions. What are the phases of the eutectic in such a case? Are they iron sulphide and manganese sulphide as might be expected? In this particular case the steel was low in sulphur (0.02 per cent) and moderately high in manganese (0.75 per cent) so that but little FeS could be expected. And since FeS and MnS form solid solutions up to at least 24 per cent FeS[4] there seems to be no probability of the inclusion containing this eutectic. Incidentally the eutectic balls up readily instead of forming the normal laminated structure. Pure FeS is not attacked by sulphur printing, it is true, but when it is present as one of the sets of plates in such a fine structure as is shown here it is all removed by sulphur printing. This must be partly mechanical. It is understandable that if only one of the sets of plates in such a fine structure were vigorously attacked by the acid the other set might readily fall out at the same time.

In Fig. 4 the effect of etching a sulphide inclusion successively with nitric and chromic acids is shown. The nitric acid brought out the ferrite envelope that is often found around sulphides but did not attack the inclusion. Chromic acid dissolved the inclusion completely but did not attack the ferrite sheath. The easy solubility indicates that the inclusion was rich in MnS and these sulphides are quite likely to be solid solutions of FeS in MnS. A portion of the ferrite envelope was carried away by the chromic acid treatment but there is no reason to believe that it was dissolved. Solution of sulphide beneath it probably left no support and it simply fell out. This bears out the suggestion of mechanical loss made above in connection with the etching of MnS-FeS eutectic.

These ferrite sheaths around sulphides are stained orange by etching in Whiteley's[5] antimony reagent. Mahin's[6] modification of the reagent is in general more satisfactory to use. It appears to be well established by Mahin's work that these ferrite sheaths are high in sulphur. They are not often seen around either oxide or silicate inclusions. An exaggerated case of such a sheath is shown in Fig. 5 and indicates that the harmful effect of an inclusion is not necessarily restricted to the actual volume occupied by it.

[4]Z. Shibata, "The Equilibrium Diagram of the FeS-MnS System," *Science Reports*, Tohoku Imperial University, Vol. 7, No. 4, 1928, p. 291-8.

[5]J. Whiteley, *Journal*, West of Scotland Iron and Steel Institute, Vol. 24, 1917, p. 79.

[6]E. G. Mahin, *Chemical and Metallurgical Engineering*, Vol. 27, 1922, p. 980.

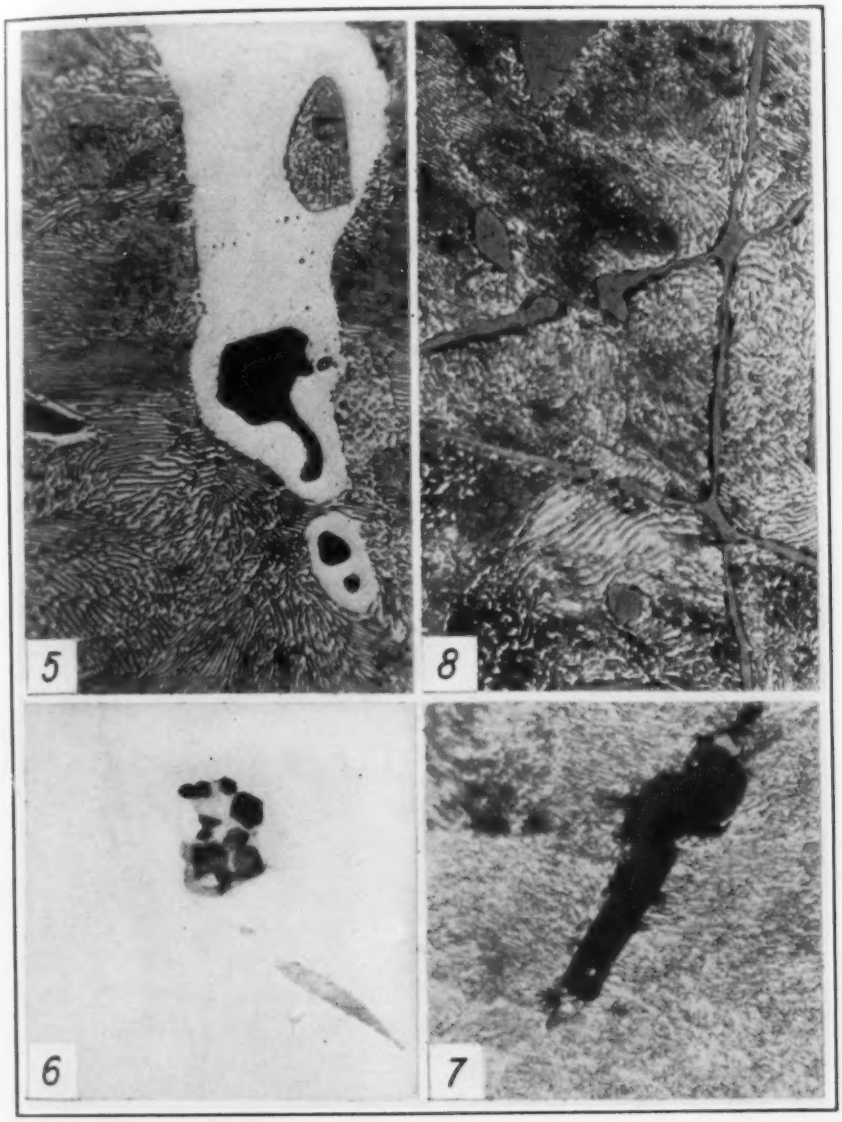


Fig. 5—Photomicrograph Showing Exaggerated Example of Ferrite Sheath Around a Sulphide Inclusion, × 1000.
Fig. 6—Photomicrograph of a Duplex Inclusion Unetched, × 1000.
Fig. 7—Photomicrograph of an Oxide-Sulphide Inclusion Etched in 10 Per Cent Nital, ×1000.
Fig. 8—Photomicrograph of Sulphide Inclusion in Cast Iron After Etching in 10 Per Cent Nital, × 500.

Fig. 6 shows what was presumably the result of several small particles coalescing to form an inclusion. The matrix was a sulphide, as shown by the chromic acid attack, but the nature of the dark crystals could not be determined as they disappeared in the etching with chromic acid, although it is extremely doubtful from their color

and crystal shape that they were sulphides. Etching tests show that these dark crystals are in most cases composed of oxides, probably solid solutions of FeO and MnO. Fig. 7 shows another inclusion of the same type but with the sulphide constituting only a small area. The bulk of the inclusion was unattacked by chromic acid etching but was deeply etched by the alkaline sodium picrate. This confirms what was suggested above that the dark material associated with the sulphide was oxide and in this steel undoubtedly rich in manganese oxide. There is a possibility that the inclusion was a silicate as sodium picrate attacks certain silicates to some extent. It will, however, be seen later that this inclusion was not typical of the silicates in this acid open-hearth steel. If it contained silica the proportion must have been very small.

Fig. 8 shows unusual sulphide inclusions in cast iron. Although this metal frequently contains as much as 0.2 per cent sulphur it is seldom that microscopic examination will show anywhere near the quantity of sulphide inclusions that would be expected from the composition. Yet on sulphur printing an extremely dark print is obtained. It is possible that much of the sulphur is associated mechanically with the graphite and is not easily found nor identified after polishing for microscopic examination. That the inclusions shown in Fig. 8 were sulphides is proved by the result of etching in chromic acid. The iron in which these inclusions were found had the following composition and was very slowly cooled from a high temperature.

	Per Cent
Total carbon	2.37
Combined carbon	0.71
Graphitic carbon	1.66
Manganese	0.78
Phosphorous	0.100
Sulphur	0.107
Silicon	0.96

Possibly the slow cooling accounts for the unusual formation of the sulphide.

Silicate Inclusions

A different type of inclusion is shown in Figs. 9 to 12. This was observed in acid open-hearth steel similar in composition to that mentioned in the discussion of sulphides. Here the attack by chromic acid was very mild and confined largely to the gray back-

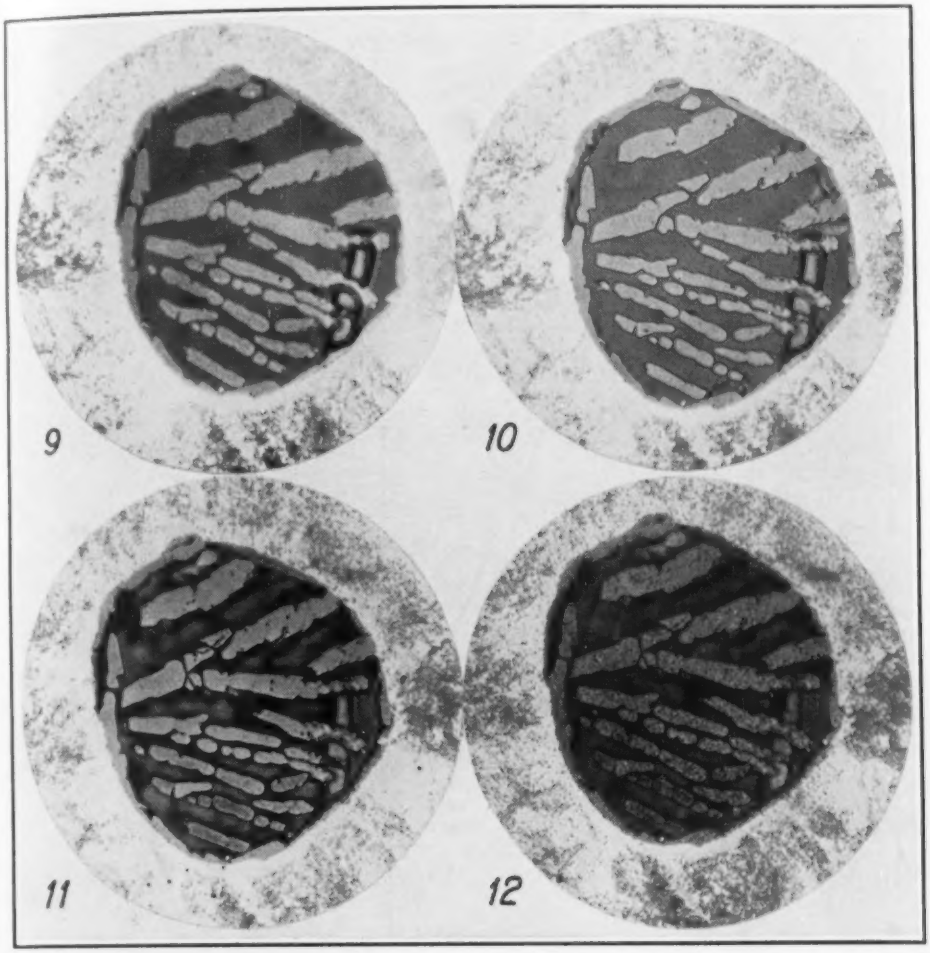


Fig. 9—Photomicrograph of Duplex Silicate Inclusion Etched in 10 Per Cent Nital, × 500.
Fig. 10—Photomicrograph of Same Specimen as in Fig. 9 After Etching in Chromic Acid, × 500.
Fig. 11—Photomicrograph of Same Specimen as in Fig. 10 After Etching in Picrate, × 500.
Fig. 12—Photomicrograph of Same Specimen as in Fig. 11 After Etching in Stannous Chloride, × 500.

ground. This inclusion did not have the usual appearance of a sulphide but may have contained dissolved sulphide. Picrate also attacked the gray background, indicating that the gray was a solid solution containing oxide and sulphide. The white needles were attacked by stannous chloride and dissolved by hydrofluoric acid, indicating an oxide-silicate complex. Fig. 13 shows an eutectic inclusion in the same type of steel after etching in sodium picrate. None of the reagents had much effect on it except hydrofluoric which dissolved it completely. It seems quite probable that two types of silicate

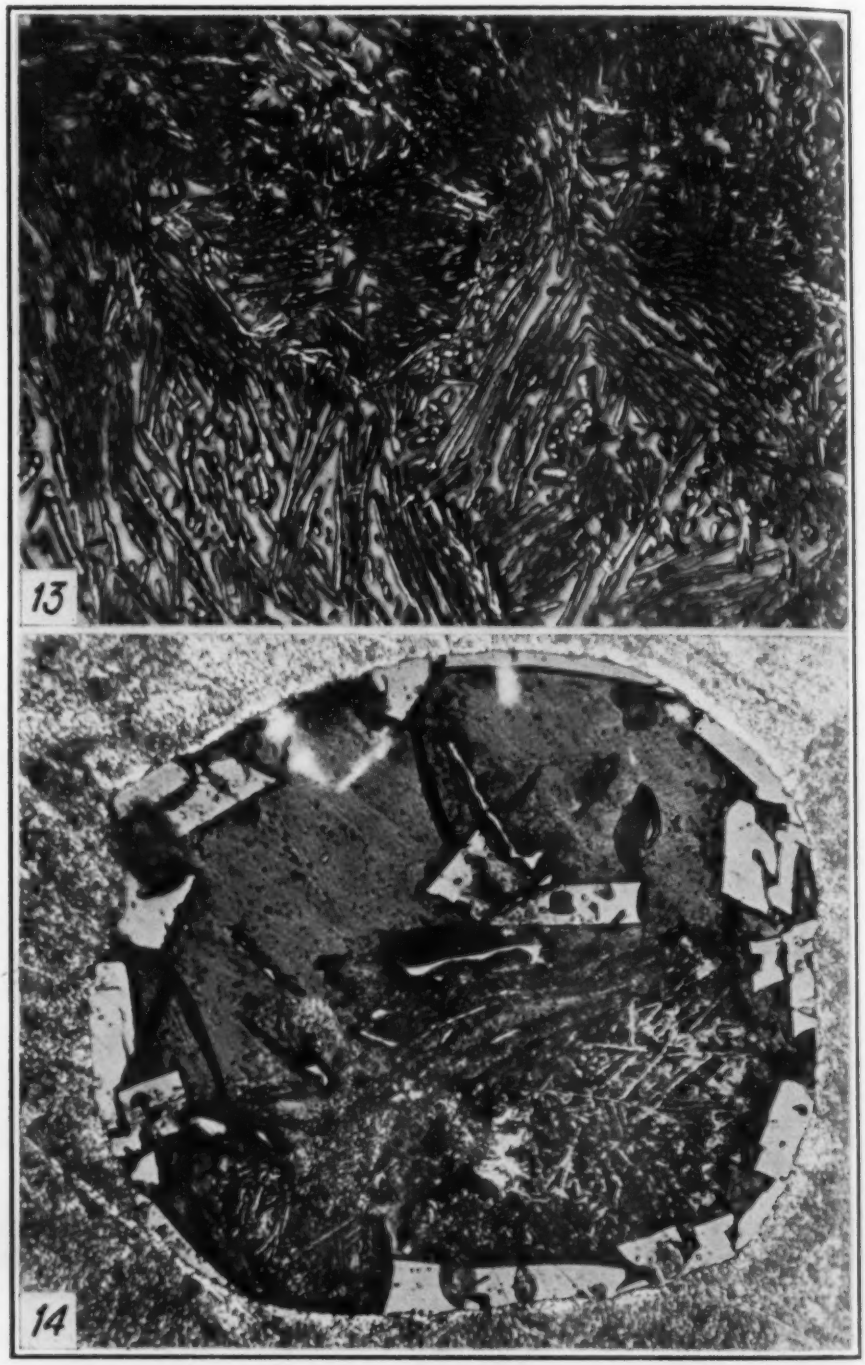


Fig. 13—Photomicrograph of Eutectic Silicate Inclusion Etched in Sodium Picrate, × 400.

Fig. 14—Photomicrograph of Complex Silicate Inclusion After Etching in Stannous Chloride, × 400.

were present in the inclusion. In acid open-hearth steel at least five primary silicates are possible. These are fayalite ($2\ FeO\text{-}SiO_2$), and tridymite, a high silica phase, in the $FeO\text{-}SiO_2$ system; and the compounds tephorite ($2\ MnO\text{-}SiO_2$), and rhodonite ($MnO\text{-}SiO_2$), and a high silica phase, also called tridymite, but having MnO instead of FeO, in the $MnO\text{-}SiO_2$ system. There are three binary eutectics and in addition there are the possible ternary phases which have not been extensively investigated. There is no ternary eutectic, however, since there is no eutectic in the FeO-MnO system. One stable ternary compound appears to exist having a composition $2\ MnO\text{-}FeO\text{-}SiO_2$[7]. In view of this it would not be surprising to find two silicates co-existing in the same inclusion and that it is not uncommon is shown by the photomicrographs Figs. 9 to 14 which are typical.

Fig. 14 shows a quite complex silicate inclusion after etching in stannous chloride. It contained sulphide, nitride, an eutectic, sharp angled crystals, similar to the white needles in Fig. 9, and a matrix rich in silica. Complete identification of such a complex inclusion could hardly be expected from a few etching tests. It is worthy of note that in this case picrate etching did not show any marked attack on the large gray areas, nor did stannous chloride attack the light sharp angled crystals. Though this inclusion was found in the same open-hearth steel as those above it seems to have differed somewhat from them. Possibly part of this difference is to be accounted for by the relatively massive form.

Examination of numerous inclusions of this type has shown that in general they are composed of at least two phases. There is a gray or dark background attacked by alkaline sodium picrate and a lighter phase unattacked by picrate but quite strongly attacked by stannous chloride. Etching, therefore, indicates that the gray contains more or less MnO while the light phase is richer in FeO. The results obtained by etching are not uniform as the phases appear to differ in the various inclusions in their resistance to the reagents. The assumption that these phases are solid solutions of variable silica content, therefore, appears justified. More selective or distinctive etching would enable more complete identification to be made.

A different type of silicate inclusion is shown in Figs. 15 and 16. This was found in the metal of a weld made between two thin low-carbon sheets by the electric arc process using a coated rod. None

[7]Herty and Fitterer, "New Manganese Silicon Alloys for the Deoxidation of Steel," Report of Investigations 3081, Feb. 1931, Bureau of Mines.

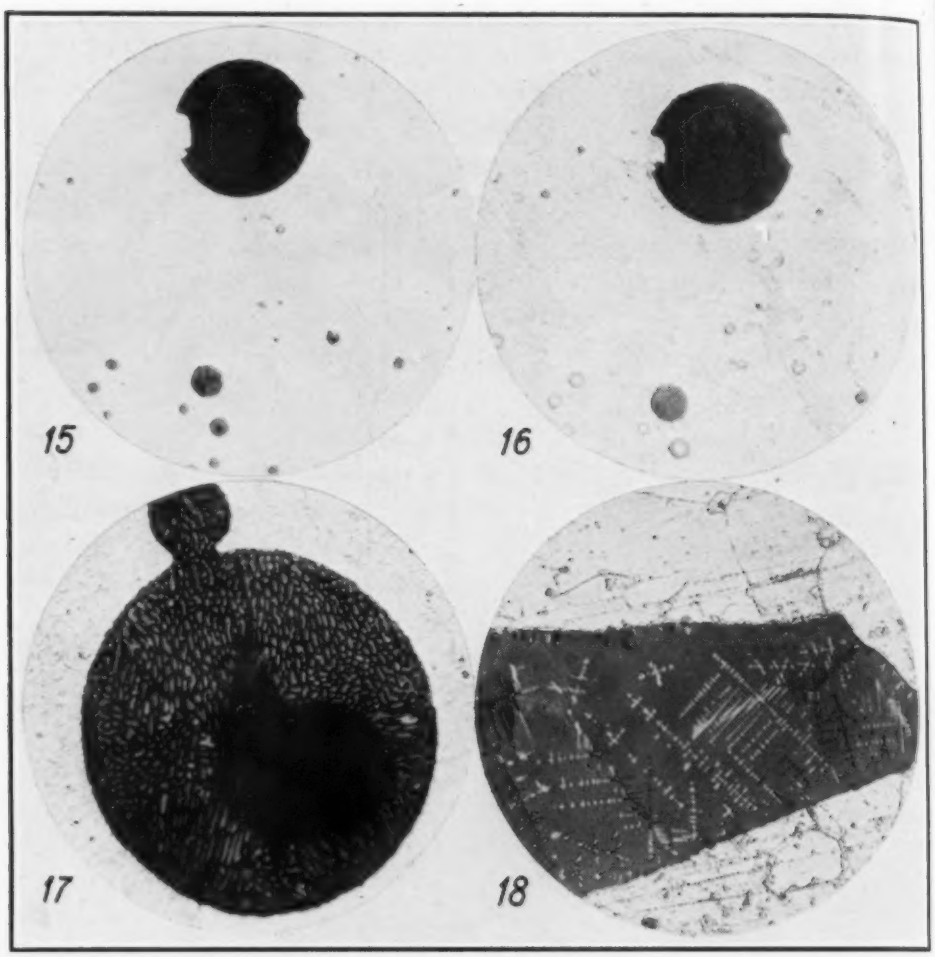


Fig. 15—Photomicrograph of a Silicate Inclusion in a Weld. Unetched. Note Evidence of Eutectic, × 1000.
Fig. 16—Photomicrograph of Same Specimen as in Fig. 15 After Etching in Stannous Chloride, × 1000.
Fig. 17—Photomicrograph of Eutectic Inclusion in a Weld. Etched in 10 Per Cent Nital, × 1000.
Fig. 18—Photomicrograph of Oxide-Silicate Inclusion in a Weld. Etched in 10 Per Cent Nital, × 1000.

of the reagents had any definite effect except hydrofluoric acid which dissolved it. It will be noticed, however, that many of the smaller inclusions around the large one were dissolved by stannous chloride. They were FeO and it is very probable that the inclusion itself carried some FeO as there was distinct evidence of a fine eutectic structure. There was a slight gain in the distinctness of the eutectic as seen in the microscope after etching in stannous chloride which would indicate that FeO was one of the phases, fayalite consequently being the other. Not all of the inclusions of this type exhibited an eutectic

but as cooling was very rapid it might well be that the structure was present but too fine to be resolved.

Fig. 17 shows another inclusion in the same weld. This showed a distinct eutectic structure, one phase of which evidently was iron oxide (FeO) as shown by the practically complete solution of the light globules in stannous cloride. Neither the background nor the light constituent was attacked by picrate etching. The conclusion seems warranted, therefore, that neither phase in this inclusion was the same as the corresponding light and dark phases in the silicate inclusions found in the acid open-hearth steel. (The dark spot near the center of the large inclusion was a pit from a previous etching and could not have been polished out completely without losing the interesting "bud" on the side.) Fig. 18 shows another interesting inclusion found in the weld. It possibly should not be classed as inclusion because it was in the junction area between the deposited metal and the sheet and consequently was more in the nature of a slag particle. It is, however, an example of what one may find in such a weld. It is not clear from the etching just how it differed from the silicates in the steel but either it was of different composition or the relatively large masses involved led to a different solution rate for the constituents. Chromic acid had no decided effect but sodium picrate attacked both the background and the light dendritic crystals. This indicates oxide or silicate or possibly both. Stannous chloride also attacked both phases, although some of the white dendrites remained after this treatment only to be dissolved by hydrofluoric acid. That two types of silicate were represented by the dendritic crystals received confirmation from the results obtained by etching another similar inclusion, Fig. 19, in the same specimen. Here also the white globular dendritic system remained after stannous chloride etching but the gray, longer dendrites were dissolved. In both inclusions all of the phases undoubtedly belonged to the FeO-MnO-SiO_2 system but the information was not sufficient to identify them completely.

Oxide Inclusions

Oxide inclusions may, if not etched, be mistaken for silicates as can be seen by the examination of the small inclusions in Fig. 15. It would be difficult to predict at this stage which were the oxides that would later be dissolved by stannous chloride. Oxides seldom are very large nor are they as numerous as the other types of in-

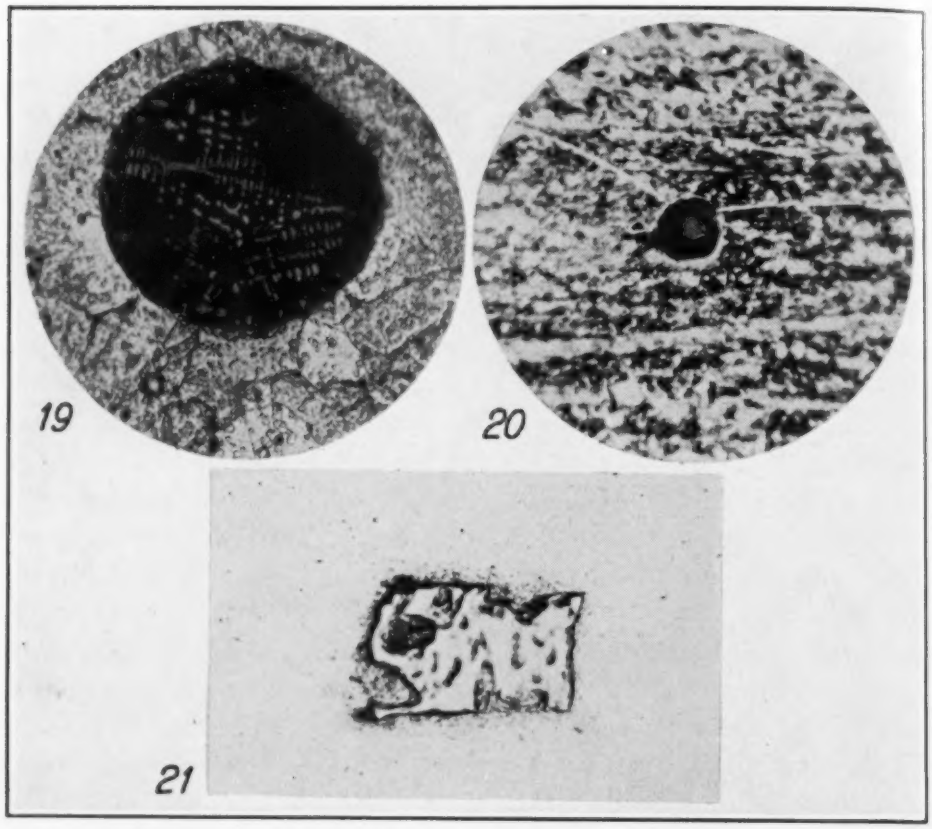


Fig. 19—Photomicrograph Showing an Inclusion with Two Silicates. Etched in Sodium Picrate, × 1000.
Fig. 20—Photomicrograph of an Oxide Inclusion in Open-hearth Iron. Etched in Sodium Picrate, × 1000.
Fig. 21—Photomicrograph of a Titanium Inclusion Unetched Showing Spots of Dark Material Associated with it. × 1000.

clusions in the majority of steels. Low carbon steels show them as very small globules similar to the one shown in Fig. 20, though this micrograph was made from a specimen of open-hearth ingot iron. None of the reagents attacked it appreciably until stannous chloride was used and then it was dissolved.

Titanium Inclusions

There seldom is any difficulty in recognizing titanium inclusions. About the only possibility of confusion is with zirconium inclusions but zirconium is not yet used enough to be of any importance in this connection. The sharp angles and distinct coloring of the titanium nitride or cyanonitride are very characteristic. The colors may range from lemon yellow, the most common color, to orange, pink,

brown, and even purple. The color probably depends on the amount of other oxides in solution in it, similar to the color of the borax beads used in qualitative analysis. Frequently there is associated with nitrides a dark spotty or finely laminated structure such as is shown in Fig. 21. Occasionally only minute yellow specks of titanium nitride will be found in these dark spots or possibly none at all but in the author's experience they are characteristic of titanium-treated steel. It has not been possible to determine whether these spotted or laminated areas are due to the titanium inclusion being polished out or are some other inclusion associated with the titanium. Although titanium inclusions are reported to be difficult to polish without pitting, the author is not inclined to accept this explanation of the spotty areas. Polishing by various methods has not supplied enough evidence to either prove or disprove the point.

Discussion

The need of further refinements in the systematic etching scheme for the identification of inclusions has been brought out above. Some means of identifying the two phases of the eutectic structure frequently associated with sulphides would be of interest. It ought not be difficult to find etching mediums that would characterize each set of laminations. Further light would undoubtedly then be thrown on the origin of such inclusions. The problem of identifying the silicates is more complex. Complete information on the ternary system FeO-MnO-SiO_2 ought to be available first as a guide. It might then be possible to distinguish the various members by etching with different concentrations of hydrofluoric acid in aqueous or other mediums. Acid or neutral solutions of fluorides might offer a means of distinguishing some of the members of the family. The production of colored compounds of manganese is another possibility, working along the lines of Whiteley's[7] reagent for sulphur.

The results shown herein for the etching of quite large inclusions indicates that they perhaps do not show normal characteristics. A longer etching period seems to be required but further investigation should be made. The rate of solubility of fine particles is always greater than the rate for large particles so that some adjustment in the temperature or time of application of the etching reagents for the large inclusions might have been anticipated. It is to be hoped,

[7] loc. cit.

however, that the occurrence of such inclusions as shown in Figs. 13 and 14 is not common in commercial steels. In basic open-hearth steel practice probably certain extensions also are required but this is outside of the field of the present paper.

Summary

1. Inclusions in steel are frequently nonhomogeneous, though moderate magnifications may be required to detect this.

2. Complete identification of the phases of nonhomogeneous inclusions cannot be made by the usual scheme used for the determination of types of inclusions.

Acknowledgments

The author desires to acknowledge his indebtedness to the members of the laboratory of the Chicago, Milwaukee, St. Paul and Pacific Railroad Co. who assisted in the work. He also extends thanks to Prof. J. E. Schoen of Marquette University for his stimulating discussion of the entire subject.

DISCUSSION

Written Discussion: By G. F. Comstock, metallurgical engineer, Titanium Alloy Mfg. Co., Niagara Falls, N. Y.

Mr. Grant's paper seems quite interesting, and the writer is glad to note that practical workers in metallography are coming to realize the value of identifying, at least roughly, the inclusions in steel. The author has shown some good photomicrographs, and well emphasizes the desirability of further work on more exact methods of identification of nonmetallic matter in steel. Some constructive suggestions from the author along that line would have been welcome, but are not found in the present paper.

It is unfortunate that the methods so far proposed for identifying inclusions have seemed to the author to imply that inclusions are always comparatively simple substances. Prof. Campbell, Dr. Wohrman, and I certainly had no such idea, and in fact expressly endeavored to point out that most inclusions are more or less complicated mixtures. The author should have omitted the word "perhaps" in his statement that the present method for classifying inclusions is claimed to be satisfactory only for making broad distinctions. It seems to me that in practical work such broad distinctions are generally most useful. If we know that an inclusion is a sulphide, for instance, it is not necessarily essential to learn the exact proportions of manganese and iron in it; nor does it matter, for practical purposes, if alumina inclusions contain also more or less iron oxide. I do not agree with the author's implied statement on page 166, line 7, that means for identifying *types* of inclusions are not now available. It seems to me that he has identified various main types very nicely.

A few comments might perhaps be offered on some of the author's photomicrographs. The black particles referred to as attached to the sulphides in Fig. 1 have often been found in our laboratory, and it was eventually decided that they were rust specks on the surface, caused by corrosion during the wet polishing. If polishing was unduly prolonged, they became larger and more numerous. Usually it was found possible to avoid them on a re-ground surface by polishing more quickly with plenty of rouge, and with a little potassium dichromate dissolved in the polishing water.

In regard to the streaked appearance of the inclusion illustrated in Fig. 3, is it not possible that the lines resembling a eutectic structure are due to reflections of light from the under surface of the inclusion? If this can be disproved, it seems more likely that they are due to oxide rather than to iron sulphide.

Fig. 20 is an extraordinary representation of ingot iron, and it would seem that some explanation is required of the structure shown by the metal surrounding the oxide inclusion. Neither nitric acid, chromic acid, nor sodium picrate should give this appearance on ingot iron if properly used. Was the sample improperly polished, or was the sodium picrate not thoroughly washed off, so that crystals of the salt remained on the dried surface? We have had both these troubles in our laboratory, and I am sorry to see such a strange illustration among the otherwise good photomicrographs of this paper.

Written Discussion: By Carl R. Wohrman, in charge of research, General Plate Co., Attleboro, Mass.

Mr. Grant has shown us a number of very interesting inclusions in commercial iron and steel.

I fully concur with the author in the viewpoint that inclusions met with in steel are far more complex than has been generally assumed;—in fact, I have taken pains to emphasize this point in my paper on "Inclusions in Iron" published several years ago.* I arrived at this conclusion largely from a study of inclusions in Armco ingot iron and of inclusions artificially prepared from known constituents, under controlled conditions. This simplified investigation to a great extent, and yet, even here, it proved difficult to identify with accuracy the phases observed. Indeed, with only sulphur and oxygen present as impurities as many as four different phases could be observed in a single inclusion. The complications bound to come in with a greater number of impurities can thus be readily understood.

Mr. Grant has been able to identify (at least in a general way) the complex inclusions he has shown us using Campbell and Comstock's modified method for identification. This can be taken as another proof of the practicability and usefulness of this method, even in the case of complex inclusions. This method, as Mr. Grant correctly remarks, is especially suited for making broad distinctions, which, in a way, is an advantage; but, without doubt, we need methods which would make finer distinctions and more accurate analyses possible. It would be highly gratifying, indeed, if some of the more chemically trained among us would take the trouble to come forward with definite and practical recommendations and instructions on this point.

I should like to call attention to Mr. Grant's Fig. 5 showing a broad fer-

*TRANSACTIONS, American Society for Steel Treating, Vol. 14, 1928, page 561.

rite sheath around a sulphide inclusion, and to his statement that this "indicates that the harmful effect of an inclusion is not necessarily restricted to the actual volume occupied by it." This may be understood to mean that the sulphide inclusion is the cause of the ferrite envelope. We cannot be quite sure of this as it is more likely that both the inclusion and the ferrite envelope are effects of the same principal cause,—segregation during solidification. As is well known, impure iron solidifies last, in the fillings of the dendrites, and is thus brought into the very same regions as the sulphide inclusions are. On cooling, the carbon diffuses away from the iron holding impurities in solution and in this manner a ferrite envelope is formed in the region of the inclusions.

Written Discussion: By G. R. Fitterer, associate metallurgist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh.

The author's major conclusion—namely, that further means for identification of impurities in steel must be devised before all of the complex materials can be detected and classified, is unquestionable. In fact, it is my belief that this line of attack in connection with the inclusion problem contains so many variables that it is hopeless. Furthermore, identification is useless without accompanying data concerning the exact furnace (and ladle) additions and conditions which caused the formation of the inclusions during manufacture. Without such additional data there would never be any hope of developing processes for eliminating such materials.

An enormous number of photomicrographs have been taken at the Pittsburgh Experiment Station of the U. S. Bureau of Mines, during the past five-year study of inclusion formation, identification, and elimination. Volumes could be written describing these materials in a manner similar to this paper but we have hesitated to publish them for two reasons:

1. Such data tend to confuse those who are not well versed in inclusion literature. (At the present time a large majority of steel inspectors have a sufficiently erroneous conception of inclusions to make it difficult for manufacturers to produce "clean" steel in future years.)

2. There are few practical instances when information regarding the composition of an individual inclusion is required. It is my belief that an accurate quantitative method of analysis is far more desirable than the ordinary visual or etch tests such as described herein. It was for this reason that the electrolytic extraction method was developed at the Pittsburgh Experiment Station of the United States Bureau of Mines. The total quantity of the separate oxides and sulphides can be determined by this method. The inclusions may be screened to various sizes and analyses of the various particle sizes made.

Sometimes it is advantageous to know if inclusions of different sizes vary widely in composition. The analyses of electrolytically extracted inclusions varying from 60-mesh (screen size) through the various standard grades to 300-mesh have been determined by the U. S. Bureau of Mines for various types of steels. Such data sometimes are very important, if it has been proved microscopically that failure was caused by particles of a given size.

It is possible that micro-methods of inorganic analysis will be developed so that an individual inclusion can be removed from the steel by electrolysis and micro-analyzed for its various constituents.

I do not agree with the author that Fig. 3 represents an inclusion. I feel certain that it is a water stain (or something of similar nature) and believe that this could be proved if the original sample were available.

Author's Closure

If one accepts Mr. Fitterer's statement that identification of inclusions is useless without data on the ladle and furnace additions then one must reject practically all of the information on the etch methods of identification as also useless. We are not prepared to do this. It is unquestionably true that quantitative analysis of the inclusions is desirable and furnishes useful information but how many metallurgical laboratories are prepared to carry out such an analysis? Furthermore the etch test is rapid and, if it can be made to give essentially the same information as would be obtained by micro-analysis of an inclusion, it certainly is preferable.

If steel inspectors have an erroneous conception of "dirty" steel it is understandable. At least much of the forging steel purchased by the railroads leaves something to be desired from the standpoint of cleanliness whether one bases his opinion on the appearance of specimens on the microscope or on the directional properties of the metal.

Fig. 3, which was commented on by both Mr. Fitterer and Mr. Comstock, shows only about one third of an elongated stringer of sulphide. It was observed in a special test specimen which was made to show whether or not bending would cause cracking of elongated inclusions. This inclusion received special attention and was examined closely both before and after the specimen had been cleaned a number of times. Many other sulphide inclusions showed small areas of the laminated structure, although space did not permit including micrographs of them. It was because laminations of this character were observed only in sulphide inclusions that we were led to believe they might be an eutectic of FeS and MnS instead of an eutectic of sulphide and oxide.

We do not believe the black spots associated with the sulphide in Fig. 1 are rust specks as suggested by Mr. Comstock. In our experience rusty spots do not have the sharp clear cut outlines shown by these spots. They were frequently found associated with sulphides. Before using dichromate in the water with the rouge for polishing we should want to be certain that it would not attack any of the inclusions.

Mr. Comstock's objection to the background in Fig. 20 appears justified. The appearance is due partly to having focussed for the inclusion only. Some roughening of the surface takes place in etching as can be seen by examination of Fig. 19, where carbonless iron also surrounds the inclusion.

Mr. Wohrman's suggestion that the ferrite sheath around sulphides may not be due entirely to the sulphur in the inclusion but partly to other impurities in solution in the ferrite has received partial confirmation by further etching tests. These envelopes are stained orange by Whiteley's reagent when the inclusion is present but they are not always similarly colored by application of this reagent after the inclusion has been dissolved by chromic acid. They are seldom seen around inclusions other than sulphides so it does not appear possible to definitely settle this point on the basis of present evidence.

PRACTICAL APPLICATION OF X-RAY DIFFRACTION METHODS IN THE STUDY OF QUENCH AND TEMPER STRUCTURES OF CARBON SPRING STEELS

By N. P. Goss

Abstract

X-ray diffraction methods show that quenching and temper structures are quite independent of each other. The X-ray spectrograph reveals in a striking manner the fact that the ill effects due to improper quenching cannot be removed by tempering. Tempering only facilitates the precipitation of the Fe_3C out of solid solution, but the as-quenched structure of the alpha iron matrix is not changed.

The X-ray can aid the metallurgist; determine the proper quench structure, and temper structure. The X-ray will show whether or not the proper quench structure was obtained though the steel may be in the tempered state.

This investigation revealed that the type of grain structure developed depends upon many factors, a few of which are: (1) Chemical composition, (2) Thickness and shape of specimen, (3) Quenching temperature, (4) Temperature of quenching medium, (5) Kind of medium (water, oil, etc.) Heating of steel which is to be quenched must also be considered. It was found that the specimens should be maintained at a constant temperature near the upper critical point, however it also depends on shape and thickness of steel. Should the steel be heated considerably above the upper critical point and then cooled down to the proper quench temperature, excessive grain distortion is developed.

THE purpose of this paper is to show how X-ray diffraction is used in studying the effects of quenching and tempering on the structures of spring steels. The methods used in this particular case may be applied to other types of steels that are quenched and tempered in order to obtain the desired physical properties.

The microscope, although giving much information about the structure of the phases present, has never been able to reveal much about the structure of the matrix, that is, the body in which the car-

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The author, Norman P. Goss, is a member of the society and is research physicist for the Cold Metal Process Co., Youngstown, Ohio. Manuscript received March 2, 1931.

bide particles are embedded. However, it has been found that if X-ray diffraction methods and the microscope are used together, the most information is then obtained. This paper will only deal with the X-ray methods because the author desires to show how these methods can be adapted to metallurgical problems of this nature. One or more typical examples are presented in order to show the research metallurgist how the problem should be carried out.

To study the structure of any quenched steel, the Laue method of X-ray crystal analysis is the most informative because it reveals the internal structure of the matrix which may be ferrite or complex solid solution. Regardless of the complexity of the crystal structure, X-rays can be depended on to reveal the true structure of the grains as well as the lattices.

In the Laue method of X-ray crystal analysis, a fine beam of small divergence is transmitted through a thin section of the specimen under investigation. In the case of low and high carbon steels, the specimen should not exceed 0.005 inches in thickness and better results appear to be obtained when the specimens are about 0.003 inches thick, although it is sometimes difficult to prepare specimens of this thickness without bending or straining them. The diffraction effects from the specimens are recorded on photographic films.

When these X-ray spectrograms exhibit radial striations, sometimes referred to as "radial asterism," then the grains of that particular metal or alloy are strained. This fact has been proven to be correct by many X-ray research workers. Glocker, in his book on "Materialprüfung Mit Roentgenstrahlen," devotes a whole chapter on this important aspect of crystals which, at the present time, seems to be much misunderstood.

As we shall see later on in this paper, the intensity of "radial asterism" seems to increase with increase in quenching temperatures but other factors also influence grain distortion. In steel in particular, at a certain temperature, the specimen may be above the upper critical transformation point while at other temperatures, it may be below the upper critical point and, of course, the grain distortion would be influenced tremendously when the quenching operation is performed from a temperature above or below the upper critical point.

It was found in one particular investigation, that the maximum hardness in some specimens of spring steel was developed when quenched from a point just above the upper critical point. The

grains were found to be free of grain distortion and the martensite was tough. This experiment also revealed that the type of quenching medium was of equal importance. In general, it was found that the high carbon steels which developed a tough martensite after quenching always give X-ray diffraction patterns free of "radial asterism."

Another interesting fact is that the hardness of these quenched steels is not influenced by grain distortion but apparently by extremely fine grain structure and lattice distortion. Some may be inclined to believe that the radial striations found in these X-ray spectrograms are related to the needles of martensite, viewed under the microscope. This is not so, for on tempering martensite the needles disappear but the radial striations on the X-ray diffraction patterns remain. This does mean, however, that tempering does not remove grain distortion but merely produces a physical change in the phase. The X-ray evidence to be presented in this paper will reveal this most interesting fact.

The X-ray patterns also show that when these specimens are quenched from a rather high temperature above the upper critical point, the diffraction rings become distorted. This means that the lattice parameters of the alpha iron are variable. In some cases, gamma iron was found to be retained and the amount present seems to be influenced by the manganese content and the temperature from which the specimen was quenched.

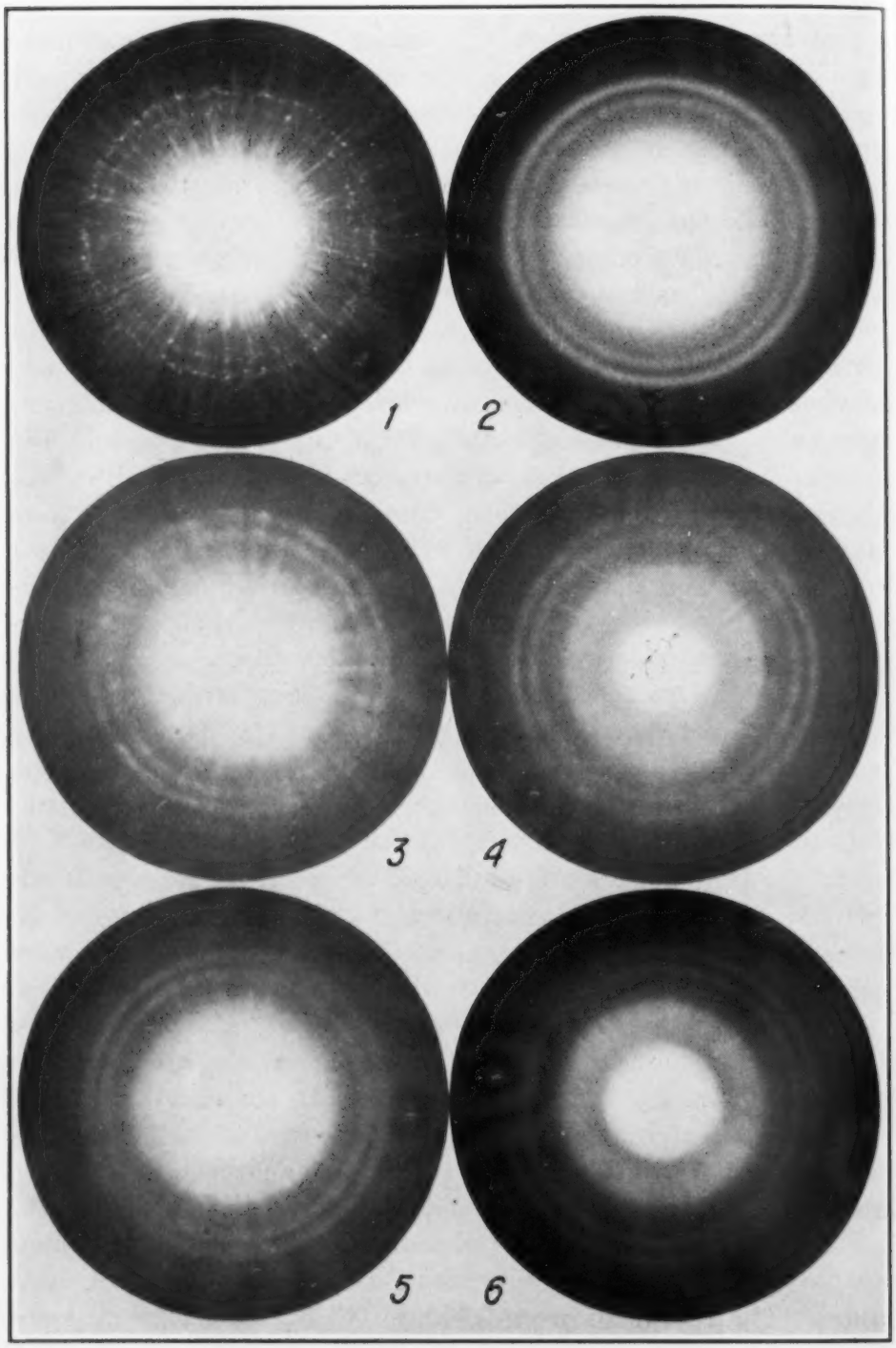
In one particular steel having a manganese content of 4 per cent and a carbon content of 0.75 per cent, annealing at as high a temperature as 1600 degrees Fahr. failed to remove the gamma iron. This illustrates the remarkable influence of small quantities of manganese in retaining gamma iron at ordinary temperatures.

In some high carbon steels of about 0.50 per cent manganese content no gamma iron was found in the as-quenched steel. Of course, in order to determine the amount of gamma iron present, it is necessary to use another X-ray diffraction method because the Laue method is not sensitive enough to detect small amounts of gamma iron. The other method used will be described later in this paper. However, it was also found that the carbon content influences the amount of gamma iron retained. In the case of 0.90 per cent carbon steel, quenched from a temperature above the upper critical point, considerable gamma iron was retained. It is evident that both manganese and carbon content along with the tempera-

ture from which the specimens are quenched influence the amount of austenite retained. Variation in lattice parameter does not mean that the lattice is distorted as it was found that on tempering such specimens, the same type of pattern resulted, showing that lattice parameter variations do not necessarily mean lattice distortion.

It is known that when gamma iron transforms to alpha iron, some carbides are thrown out of solid solution because gamma iron can hold more carbon in solution than can alpha iron. This may bear some relationship to the lattice parameter variations as indicated on some of the X-ray spectrograms. It was always found that whenever the specimens were heated to a high temperature and quenched, such variations were always found. It is rather interesting to know that when one specimen, the X-ray pattern of which will be shown later, was heated to 1800 degrees Fahr. and cooled to 1420 degrees Fahr. and then quenched, lattice parameter variations were still present, even though the specimen was quenched from the proper temperature. This illustrates that in order to eliminate lattice parameter variations, the specimens must not be heated above the temperature from which they should be quenched.

The X-ray patterns, therefore, show that lattice parameter variations are not changed by tempering. This is a most interesting fact. Some metallurgists may believe that the tempering operation removes grain distortion but this is not so. It merely removes internal lattice distortion which is facilitated by the precipitation of the carbide from solid solution, that is, when martensite transforms to sorbite. The X-ray patterns also show that the structures of all these steels are extremely fine-grained. Whenever intensity maxima appear on the diffraction patterns which represent quenched steels, it merely means that the austenite grains prior to quenching were quite large and that during the transformation of gamma iron to alpha iron, the newly formed alpha iron tends to retain the orientation of the parent iron grain. The specimens used in this investigation were heated in a small electric furnace and held at that temperature for about ten minutes and quenched. This was thought necessary so as to be sure that the carbon would be in solid solution with the gamma iron before quenching and to insure thermal equilibrium. The specimens were 0.625 to 0.028 inch thick and were about three to four inches in length having a manganese content of 0.70 per cent and a carbon content of 0.61 per cent. They were heated and quenched in oil and water. The quenching temperatures



X-RAY DIFFRACTION PATTERNS

Fig. 1—0.60% Carbon, 0.70% Manganese Steel Annealed at 1200° F.

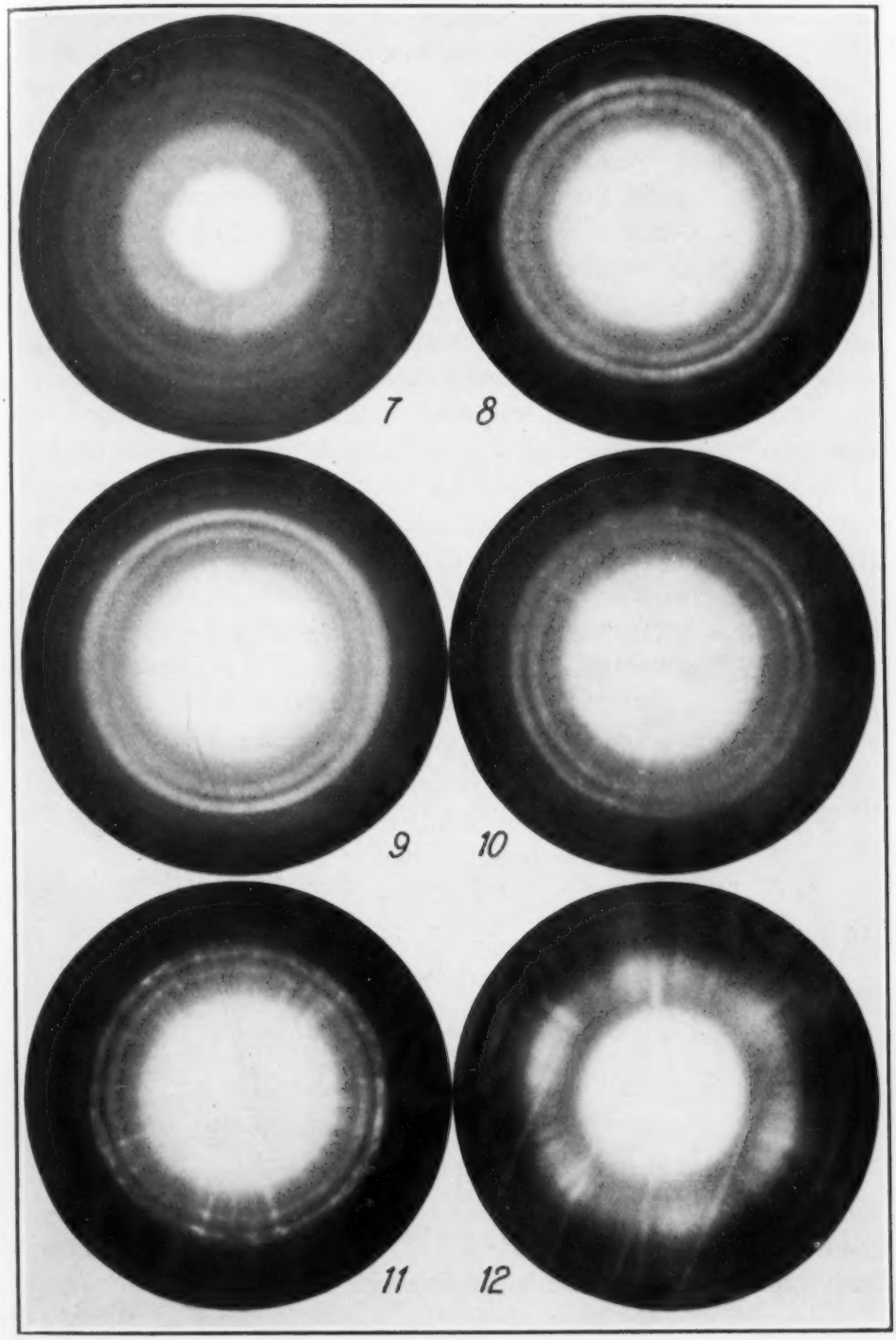
Fig. 2—0.64% Carbon, 1.35% Manganese Steel Oil-Quenched after 15 Minutes at 1410° F.

Fig. 3—0.70% Carbon, 1.02% Manganese Steel Heated to 1900° F. Cooled to 1420° F. in 13 Minutes, held there 1 minute, then Quenched in Oil at 70° F. Rockwell C 56 to C 59.

Fig. 4—0.60% Carbon Steel Oil-Quenched After Heating 10 Minutes at 1800° F.

Fig. 5—Medium Carbon Steel Water-Quenched After Heating 15 Minutes at 1800° F.

Fig. 6—0.60% Carbon Steel Oil-Quenched After Heating 10 Minutes at 1400° F. Rockwell C 62.



X-RAY DIFFRACTION PATTERNS

Fig. 7—0.60% Carbon Steel Water-Quenched After Heating 10 Minutes at 1400° F. Rockwell C 63.

Fig. 8—0.60% Carbon, 0.70% Manganese Steel Oil-Quenched at 180° F. After Heating at 1450° F. Rockwell C 60-61.

Fig. 9—0.61% Carbon, 0.70% Manganese Steel. (1) Pot-annealed at 1250° F. (2) Area Reduction 20%. Heated at 1450° F. Quenched in Oil at 400° F. Rockwell C 59.

Fig. 10—0.61% Carbon Steel. (1) Pot-annealed at 1250° F. (2) Area Reduction 40%. (3) Oil-Quenched from 1800° F. Rockwell C 60.

Fig. 11—0.64% Carbon, 1.35% Manganese Steel Water-Quenched from 2000° F. Rockwell C 40-50.

Fig. 12—0.60% Carbon Steel, Water-Quenched from 1950° F.

used in this test were 1350, 1400, 1450, 1600 and 1800 degrees Fahr.

The flat wire specimens were in the annealed condition, the temperature of annealing being between 1200 and 1250 degrees Fahr. Fig. 1 is the Laue X-ray pattern of this wire. It can be seen that the ferrite and pearlite are in a strained state because the pattern indicates lattice parameter variations and this, of course, is to be expected since we are dealing with a mixture of pearlite and ferrite.

It was found necessary in steels having a high manganese content (1 to 1.5 per cent is considered a high manganese content for spring steel), to quench from a temperature just above the upper critical point. This is illustrated in Fig. 3. It shows that the temperature to which a given specimen may be heated has a marked influence on the as-quenched structure, even though it was quenched from the proper temperature. When high manganese steels are quenched from extremely high temperatures, excessive quenching strains or grain distortions are developed but when these steels are properly quenched an ideal structure is developed. Figs. 2 and 3 illustrate this. The Laue pattern shown in Fig. 2 was made from steel containing 0.64 per cent carbon and 1.35 per cent manganese. It was heated to 1400 degrees Fahr. and held there for fifteen minutes and oil-quenched. The X-ray pattern shows that:

(1) The grains are distributed at random,
(2) The grains are very small,
(3) The grains are not distorted,
(4) The lattice parameter is very uniform. (Diffraction rings are not distorted)

The Laue X-ray pattern shown in Fig. 3 was made from a steel containing 0.70 per cent carbon and 1.02 per cent manganese. It was heated at 1900 degrees Fahr. and cooled to 1400 degrees Fahr. in fifteen minutes and held at that temperature for one minute after which it was oil-quenched. The X-ray spectrogram shows that:

(1) Grain distribution is not random,
(2) Grains are distorted,
(3) Lattice parameter is variable.

Such a quenched structure is far from ideal.

From a consideration of Figs. 2 and 3, it seems as though the high manganese carbon spring steels are superior in structure to the high carbon, low manganese spring steels but they must be quenched under the proper conditions. Other investigators report that man-

ganese improves the mechanical properties of steel and the X-ray evidence submitted supports this contention. (TRANSACTIONS) July, 1928. When quenched from 1600 degrees Fahr. in oil and water, it was found that the grains were not only distorted but were not distributed at random. Greater distortion was produced when the specimens were quenched in oil and water from 1800 degrees Fahr. The X-ray patterns shown in Figs. 4 and 5 illustrate this.

It will be quite interesting to study the quenched structure of specimens quenched in oil and water from 1400 degrees Fahr. and Figs. 6 and 7 show the X-ray spectra obtained from such structures. Apparently it makes no difference whether these specimens were quenched in oil or water from 1400 degrees Fahr. because the X-ray spectrograms are quite similar. A photomicrograph was made and it showed the needles of martensite to be quite short and massive. In fact, Figs. 6 and 7 look like Figs. 4 and 5 except that the diffraction rings are not quite as spotted or streaked. Does this mean that the quenching is too drastic for this size specimen? It would not be possible to quench from a much lower temperature than this because the steel would not harden. The only thing that remains to be done is to heat the quenching medium to high temperatures.

The oil and water quenching baths were kept about 80 degrees Fahr. but the temperature of these baths was then increased to 180 degrees Fahr. and the steel specimens were heated to 1450 degrees Fahr. after which they were quenched in oil at this temperature. Fig. 8 shows the result of this treatment. The diffraction effects are much more intense. In fact, the diffraction from the (2 1 1) planes is much more marked but the "radial asterism" is still evident and this means that the grain structure is distorted and the grains are not distributed at random. The question at once arises, can distorted grain structure be eliminated? Perhaps an increase in temperature of the oil bath might accomplish this. It was found that when the oil bath was heated to 400 degrees Fahr. and the specimen (0.023 inch thick) was heated to 1450 degrees Fahr. and quenched in this oil, grain distortion was eliminated. Hardness measurements were made and it was found that it had a uniform hardness of Rockwell C59, the quenching medium being engine oil.

A microscopic examination showed that the structure was still martensitic. Fig. 9 is the spectrogram of one of these specimens and it is at once apparent that grain distortion has been entirely eliminated by this practice of heat treatment. This means that the

type of grain structure developed depends upon many factors of which a few are:

(1) Chemical composition,
(2) Thickness and shape of specimens,
(3) The quenching temperature,
(4) The temperature of the quenching medium, and
(5) The kind of medium.

In order to again show the effects of quenching from a high temperature in oil at room temperature another specimen was heated to 1800 degrees Fahr. and quenched. The X-ray spectrogram is shown in Fig. 10. Here again the grains are distorted and lack random distribution. That the grains should be distributed at random is a most essential structure requirement. Even greater grain distortion is possible and it is with this in mind that the next group of X-ray patterns are shown.

Fig. 11 is an X-ray spectrogram of a steel containing 0.64 per cent carbon and 1.35 per cent manganese heated to 2000 degrees Fahr. and quenched in water. Besides the distorted grain structure, a considerable amount of gamma iron was retained and this accounts in part for the low Rockwell hardness number (C 40 to 50) for this drastically quenched specimen. When this particular specimen was drawn at 500 degrees Fahr., the hardness increased, due to a decomposition of the austenite.

Another X-ray spectrogram of a steel containing 0.60 per cent carbon heated to 1950 degrees Fahr. and water-quenched is shown in Fig. 12. Note the extreme distortion of the grains and it also shows that the austenite grains were large prior to quenching. In fact, this pattern suggests a kind of a fiber structure, in that, the radial streaks appear to be grouped into six distinct spots which is characteristic of a fiber pattern.

As already noted above, tempering will not remove grain distortion and distribute the grains at random. A 0.64 per cent carbon steel wire, quenched in water from 1900 degrees Fahr. had a Rockwell hardness of C 64. It was then tempered at 850 degrees Fahr. for fifteen minutes, the Rockwell hardness tested to C 44 to 45. Fig. 13 is the X-ray pattern of this tempered structure and clearly shows that the tempering operation did not change the structure of the alpha iron matrix. Why we have a decrease in hardness is well known because on tempering martensite to sorbite, a precipitation

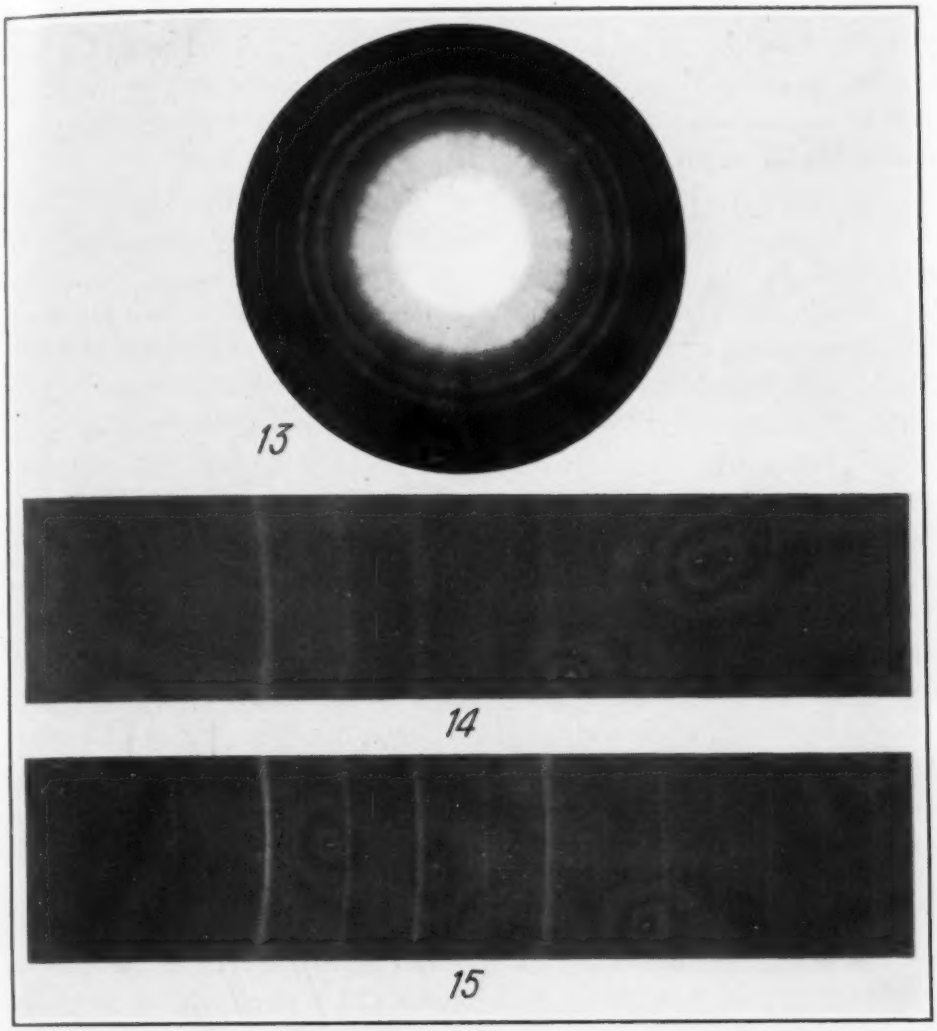


Fig. 13—X-ray Diffraction Pattern of a 0.60 Per Cent Carbon Steel, Heated at 1900 Degrees Fahr. and Water-quenched. Rockwell C64 and then Tempered at 850 Degrees Fahr. for 15 Minutes. Rockwell C44-45.

Fig. 14—X-ray Diffraction Pattern of the Reflection Type Taken of a 0.64 Per Cent Carbon, 1.35 Manganese Steel, Heated at 1420 Degrees Fahr. for 15 Minutes and Quenched in Oil.

Fig. 15—X-ray Diffraction Pattern of the Reflection Type Made of the Same Specimen as Shown in Fig. 14 Except that this was Made of the Specimen Tempered at 880 Degrees Fahr. for 15 Minutes.

of Fe_3C takes place in which the sorbite is considered to be an emulsion of Fe_3C in alpha iron. The tempering temperature of 850 degrees Fahr. is favorable to the transformation of martensite to sorbite. The X-ray pattern clearly shows that the tempering did not change the structure of the alpha iron matrix because it is still distorted and the alpha iron is not distributed at random so we can conclude that tempering does not remove grain distortion due to improper quenching but that tempering only facilitates the transfor-

mation of martensite to sorbite, but this change no doubt removes lattice distortion. The Laue method of X-ray crystal analysis does not tell us much about this structure transformation and so the question at once arises, can the X-ray diffraction method detect the transformation of martensite to sorbite.

In order to show the effect of tempering on high carbon steel wires, it is necessary to use an entirely new X-ray technique. In this method, the fundamental idea is the resolution of the $K\alpha$ "doublet." It has been shown that whenever these lines are resolved, the crystal lattice is free of atomic distortion, that is, variations in lattice parameters. A distorted lattice is due to internal strains within the lattice itself. Fig. 14 is an X-ray spectrogram of such an as-quenched high carbon wire. It will be noted that the lines are rather broad and somewhat diffuse and this means that the grains are built up of molecules which have small variable lattice parameters due to internal strains. It was also found that the grains are extremely small. The diffusion then is due to two things; small grain size and dilation of the alpha iron lattice which is due to the carbon atoms scattered at random in the space lattice. Fig. 15 is the X-ray spectrogram of the same specimen after it has been tempered at 880 degrees Fahr. for fifteen minutes. It shows that the tempering operation has completely removed lattice distortions since the $K\alpha$ lines are sharp and resolved. However, the grains are still small.

In martensite the carbon atoms are considered to be atomically dispersed in the ferrite and this may be the reason the diffraction lines in the X-ray spectrogram are rather broad and diffuse. On tempering the carbon atoms precipitate and form Fe_3C during the precipitation. This causes the ferrite atom to assume its normal dimensions. The structure of the ferrite grains is not changed, during this transformation. The tempering operation only causes a phase change, in that, the martensite transforms to sorbite but the structure of the alpha iron grains remain unchanged.

This experiment has shown then that quenching structures and tempering structures are independent of one another, that tempering does not remove the ill effects that may be due to improper quenching of any steel but that the tempering operation merely facilitates a physical change in the phase.

It was found that grain distortion cannot be detected by hardness measurements but that whenever specimens free of grain distortion were produced, the martensite was much tougher.

SCALING OF STEEL AT ELEVATED TEMPERATURES BY REACTION WITH GASES AND THE PROPERTIES OF THE RESULTING OXIDES

By D. W. Murphy, W. P. Wood and W. E. Jominy

Abstract

This paper presents the results of an investigation of the variables affecting the oxidation of steel in the temperature range 1095 to 1315 degrees Cent. (2000-2400 degrees Fahr.) and shows that the effect of complex atmospheres on steel may be predicted from a knowledge of the equilibria in the systems Fe:O:C and Fe:O:H. The results of this research may be summarized in accordance with the following:

1. The loss in weight of the metal due to scaling is proportional within limits to the area of the sample,

2. The effect of increasing the carbon content in the range 0.3 to 1.1 per cent decreases the scaling losses,

3. The scaling loss is lessened by a slow rate of the flow of gas,

4. The rate of oxidation decreases as the time of exposure increases,

5. The extent of oxidation depends on the relative rates of diffusion of the gases concerned in the reaction,

6. A new method has been applied to the determination of equilibria in the reactions, $FeO + H_2 \rightleftarrows Fe + H_2O$ and $FeO + CO \rightleftarrows Fe + CO_2$ in the temperature range of 1095 to 1425 degrees Cent. (2000 to 2600 degrees Fahr.),

7. The melting point of ferrous oxide was determined from the data on the two systems at 1360 ± 10 degrees Cent. (2480 ± 18 degrees Fahr.),

8. The heat of fusion of ferrous oxide was calculated as 28,000 calories per gram mol ± 5000 calories,

9. X-ray data have shown that ferrous oxide is

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A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The authors are members of the society. D. W. Murphy is associated with the Department of Engineering Research, University of Michigan; W. P. Wood is professor of metallurgical engineering, University of Michigan; and W. E. Jominy is connected with the research department of the A. O. Smith Corp., Milwaukee. Manuscript received June 15, 1931.

stable above its melting point having a constant 4.289 A. U. both above and below the melting point,

10. No evidence of extensive solid solutions of Fe or of Fe_3O_4 in FeO was obtained in this investigation,

11. The scaling or non-scaling action of a gas atmosphere containing nitrogen, carbon dioxide, carbon monoxide, hydrogen, and water vapor may be predicted with considerable accuracy for a number of steels on the basis of the equilibrium ratios derived for the two systems Fe: FeO: CO: CO_2 and Fe: FeO: H_2: H_2O.

THE oxidation of steel or iron by reaction with gases is an interesting problem for both theoretical and applied research. A considerable amount of work has been done in connection with this general problem but in the main the results have shown a lack of concordance. In most cases such data as were available were obtained at temperatures below 1035 degrees Cent. (1900 degrees Fahr.) which is under the temperature ordinarily used in forging practice. The present research was undertaken at the instigation of The American Gas Association for the purpose of thoroughly investigating the scaling of steel throughout the complete forging range. The problem has naturally divided itself into two parts:

(a). The investigation of the variables which control the process of continuous oxidation; namely, velocity of the gas stream, time, temperature, and gas composition. In addition a brief study was made of the effect of chemical composition on the scaling of steel particularly with reference to carbon.

(b). The determination of equilibria in the systems Fe: FeO: CO: CO_2 and Fe: FeO: H_2: H_2O from which the effect of any gas-air combustion atmosphere can be predicted. In this connection various steels were subjected to scaling and non-scaling atmospheres, and the effects of these atmospheres were compared with those theoretically deduced from the equilibria determinations in order to prove definitely that the direction of the effect of the gas-air combustion atmosphere on steel may be predicted from the analysis of the atmosphere.

Review of Literature

Previous investigations of the oxidation of iron and ferrous alloys fall into three general classes. The first and oldest of these is concerned with the determination of the various equilibria in the

systems Fe:O:H and Fe:C:O. The second class includes a number of more or less empirical researches whose object generally was to ascertain the oxidizing effect of various gases, chiefly air on specific metals. Such researches have for the most part entirely disregarded many of the variables which enter into the oxidation process. The third class of investigations are those few in which attempts were made to deduce possible mechanisms for continued oxidation. In the latter two classes the variables considered have been limited in number, and no thorough study made of these factors.

The first published record of investigations in these systems was that by Deville[1] in 1870. He studied the qualitative aspects of the system Fe:O:H. The method first employed by Deville and some later investigators consisted essentially of heating iron-iron oxide mixtures in a porcelain or quartz tube in contact with the gas phase in a sealed system until equilibrium was reached at a constant temperature.

In the case of H_2:H_2O equilibria the reaction tube containing the solid phases was connected with a reservoir containing water maintained at a constant temperature. The tube was evacuated to a pressure corresponding to the vapor pressure of water at the reservoir temperature. The reaction of steam and iron produced hydrogen which caused an increase of pressure in the system, which change in pressure was observed by means of a manometer which registered the total pressure. Heating at constant temperature was continued until the total pressure given by the manometer remained constant when equilibrium was considered to have been established. From the known vapor pressure of water and the total pressure in the system, the pressure and consequently the percentage of hydrogen were calculated. In the case of the Fe:O:C system the gas phase, carbon dioxide, or carbon monoxide, depending on the desired direction of approach to equilibrium, was introduced into an evacuated tube containing the solid phase until atmospheric pressure was attained. After certain periods of time, samples of gas were withdrawn and analyzed; equilibrium was considered as established when no variation in composition occurred with increasing time.

Eastman[2] in 1922 reviewed the available literature in the Fe:O:H and Fe:O:C systems. He noted that in general the results of preceding investigations of the Fe:O:H system fell into two groups

[1]Deville, *Comptes Rendus*, Vol. 70, p. 1105, 1210 (1870), also Vol. 71, p. 30 (1870).

[2]Eastman, *Journal*, American Chemical Society, Vol. 44, 1922, p. 975.

differing by as much as 40 to 50 per cent in values of the equilibrium constant, and yet there appeared to be little reason for choosing one set in preference to the other on the basis of experimental procedure. Consideration of this system in conjunction with the Fe:O:C system led Eastman to postulate the existence of solid solutions over a considerable range of oxygen content instead of definite constant solid phases as an explanation of the discrepancies existing between the two groups of data. Later his investigation with Evans[3] seemed to confirm those showing high values of the constant. The apparent reliability of his results with the Fe:O:H system led to questions concerning the reliability of the accepted constants for the water-gas reaction as determined by Haber,[4] Hahn,[5] and others when his data were combined with data on the Fe:C:O system in the indirect calculation of these constants.

Neumann and Kohler[6] in 1928 in a careful and thorough research on the direct determination of the water-gas equilibrium, established the constants of that reaction with considerable precision, and agreed substantially with the previous direct determinations. The results of the indirect calculation from the Fe:C:O and Fe:O:H systems pointed to weaknesses in the Fe:H:O determinations. The work of Krings and Kempkens,[7] of Tritton and Hanson,[8] and of Herty,[9] which has definitely limited the possible solid solutions of Fe and FeO has seemed to disprove the possibility of extensive solid solutions as an explanation of the discrepancies existing in the data on the Fe:O:H system.

Emmett and Schultz[10] in 1930 published the results of their research in which a flow method somewhat similar to that of Ferguson was used. Their method consisted of passing steam-hydrogen mixtures over iron-iron oxide mixtures and then collecting the effluent gases for a certain period of time and determining the relative

[3]Eastman and Evans, *Journal*, American Chemical Society, Vol. 46, 1924, p. 888.

[4]Haber, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 38, 1904, p. 5.

[5]Hahn, *Zeitschrift fuer Physikalische Chemie*, Vol. 44, 1903, p. 5131 and Vol. 48, 1904, p. 735.

[6]Neumann and Kohler, *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, Vol. 34, 1928, p. 218.

[7]Krings and Kempkens, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 183, 1929, p. 225.

[8]Tritton and Hanson. *Journal* Iron and Steel Institute, Vol. 110, 1924, p. 85.

[9]Herty, et al. "Physical Chemistry of Steel Making," Carnegie Institute Technology, Bulletin 34, 1927.

[10]Emmett and Schultz, *Journal*, American Chemical Society, Vol. 52, 1930, p. 4268.

quantities of water and hydrogen. The analyses were repeated many times at each temperature starting with steam-hydrogen mixtures for both reducing and oxidizing conditions and thus a high degree of accuracy was insured. The excellent agreement of their work when combined with data on the Fe:C:O system in indirect calculation of the water-gas constants with the direct determinations of Neumann and Kohler, seems to be proof of the validity of their work.

Eastman,[2] found that the data on the Fe:C:O system were somewhat more concordant than in the Fe:H:O system. He placed much weight on the determinations of Matsubara[11] in spite of the questionable temperature measurements of that author. Garran[12] attempted to carry the experimental data to a temperature of 1300 degrees Cent. (2370 degrees Fahr.) but impurities in the iron made his work doubtful. Schenck,[13] in a series of papers, reported the results of extensive determinations in this system. He pointed out that a considerable number of impurities have a decided effect on the equilibria in this system, and his work shows that where these have not been considered the results are of very questionable value. In view of the care with which this research has been carried on and the general consistency of his results it seems quite likely that his recent data are the most acceptable that has yet appeared.

The empirical researches which were chiefly concerned with oxidation of specific materials are quite numerous. The data presented in these empirical researches are not extremely concordant and include a number of scattered observations. The early authors, Scott,[14] McCormick,[15] Stead,[16] and Dickenson,[17] used crude methods for determining the extent of oxidation; scale was removed by abrasion which must, of course, have removed also an indeterminate quantity of iron; conditions of purity of gases, temperature control, and other factors such as the velocity of the gas stream were inade-

[11]Matsubara, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 67, 1922, p. 3.

[12]Garran, *Transactions*, Faraday Society, Vol. 24, 1928, p. 201.

[13]Schenck, et al., *Zeitscrift fuer Anorganische und Allgemeine Chemie*, Vol. 167, p. 315; Vol. 166, p. 113; Vol. 167, p. 254, 1927.

[14]Scott, *Chemical and Metallurgical Engineering*, Vol. 25, 1921, p. 72.

[15]McCormick, TRANSACTIONS, American Society for Steel Treating, Vol. 2, 1922, p. 1006.

[16]Stead, *Journal*, Iron and Steel Institute, 1916; *Engineering*, Vol. 102, 1916, p. 367.

[17]Dickenson, *Journal*, Iron and Steel Institute, 1922; *Engineering*, Vol. 114, 1922, pp. 326-9.

quately controlled. The later authors, Cobb[18] and his associates, Utida and Saito[19] and Hatfield,[20] based their measurements on gain in weight, a more reliable method although it fails to give a clear conception of the quantity of metal lost since the oxides may vary in composition under different conditions of temperature and atmosphere and with different compositions of original material. Furthermore, most of these results are rendered incomparable since one variable, velocity of the gas stream, has been almost wholly neglected.

Attempts to outline a possible mechanism for continued oxidation of a metal, form the third class. Jordis and Rosenhaupt[21] in 1908 advanced the following hypotheses to explain surface oxidation: (a) The oxygen may dissolve in the metal as such or as an alloy; (b) the oxygen may diffuse through the layer of oxide which may dissolve the oxygen or merely be porous to it; (c) oxygen may be carried by the alternate formation of higher and lower oxides; or (d) the oxide may fall from the surface of the metal. Most of the ideas subsequently advanced by other authors are in support of one of these hypotheses. Friend[22] advanced the hypothesis that oxidation in the case of steam was carried on in the following manner. Steam first dissociates into hydrogen and oxygen. The oxygen thus liberated, oxidizes the metal to FeO and later to Fe_3O_4. Oxidation continues by alternate reduction and formation of this latter oxide.

Pilling and Bedworth[23] studied rather extensively the oxidation of copper in air at various temperatures and for various times. They classified metals as noble or base, depending on the magnitude of the dissociation pressure of the oxide which for the noble metals is so high even at low temperatures as to preclude oxidation. The base metals they divide into two groups depending on the oxide texture which determines whether or not the oxide coating will retard further oxidation. They interpreted their data as showing that continued oxidation of a metal resulted from the solution and diffusion of oxygen through the oxide layers. Their work was incomplete

[18]Cobb, et al., *Journal*, Society of Chemical Industry, Vol. 46, 1927, p. 61 T, p. 68 T.

[19]Utida and Saito, *Science Reports*, Tohoku Imperial University, Vol. 13, 1925, p. 391.

[20]Hatfield, *Journal*, Iron and Steel Institute, 1927, p. 483.

[21]Jordis and Rosenhaupt, *Zeitschrift fuer Angewandte Chemie*, Vol. 21, 1908, p. 50.

[22]Friend, *Journal*, Iron and Steel Institute, Vol. 80, 1909, p. 172. *Journal*, West Scotland Iron and Steel Institute, Vol. 17, 1910, p. 66. *Proceedings*, Chemical Society, Vol. 27, 1911, p. 124. *Journal*, Chemical Society, Vol. 99, 1911, p. 969.

[23]Pilling and Bedworth, *Journal*, Institute of Metals, 1923.

since they did not consider the velocity and composition of the gas.

Fedotjev and Petrenka[24] favor the transfer of oxygen by means of the alternate formation of higher and lower oxides. According to this mechanism one of the higher oxides, Fe_2O_3 or Fe_3O_4 is first formed, and this is subsequently reduced by the iron in contact with it to FeO, additional iron being oxidized in this process. The FeO is then oxidized to a higher oxide and the reaction continues.

Pfeil[25] in 1930 published an account of his experiments as a result of which he advanced the idea that in addition to oxygen diffusing inward through the scale, iron in some form must also diffuse outward. He also established the fact that two scales of different oxygen contents can react even when not actually in contact with each other. As proof that there must be a diffusion of iron outward, he cited the following facts. The scale as it forms begins to surround foreign objects and may eventually cover them up without, however, disturbing their initial position; the original markings on the test samples are preserved in relief on the middle portion of the scale in the same position they had on the original sample. These facts taken in conjunction, preclude any possibility of plastic flow to account for growth of the scale outward, and the diffusion of iron will explain the development of the large oxide crystals in some cases. As the mechanism exists now, continued oxidation is accompanied by a diffusion of iron outward and a migration of oxygen inward. This latter seems to occur partially as a result of the ability of scales or oxides of differing oxygen content to react with each other. This hypothesis seems to be the most acceptable in view of the facts as understood at present. There were some facts brought out in the present research which seemed to indicate that some modification of this hypothesis was necessary.

In concluding this survey of the literature it would be well to summarize a few points concerning the past work. There are no accurate data on the equilibria in the system Fe:C:O above 1100 degrees Cent. (2010 degrees Fahr.) and none above 1000 degrees Cent. (1830 degrees Fahr.) in the system Fe:O:H. While extrapolation of data obtained at lower temperatures would be fairly reliable up to the melting point of the oxide, extension beyond this point involves guessing at the probable heat of fusion of the oxide.

[24]Fedotjev and Petrenka, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 157, 1926, p. 165.

[25]Pfeil, *Journal*, Iron and Steel Institute (1930).

Furthermore, there has been no systematic investigation of the various factors which influence the process of scaling. It was hoped that this investigation would serve to bring these factors into proper relation to each other, and indicate a comprehensive mechanism.

Procedure

The apparatus used in this study is in most respects similar to that used by other investigators. The methods employed in the conduct of tests, however, differ considerably from those used previously. Both have been described in previous publications but a brief resumé will be of value.

Apparatus

The heating equipment used in this research consisted of a gas-fired muffle furnace in which a glazed porcelain tube having a 2-inch inside diameter was placed in such a manner that both ends of the tube projected some distance beyond the furnace walls. One end of the tube was fitted with an asbestos plug through which there were two holes, one for the thermocouple protection tube, and one for the introduction of the chosen gas. This plug was capped and held in place with firebond cement which produced a tight joint. The other end of the tube through which the sample was introduced was provided with a rubber stopper since this end was sufficiently cool to prevent any decomposition of the stopper. Two types of thermocouple protection tubes were used, a sillimanite tube and a glazed closed-end porcelain tube. The thermocouple and its protection tube were so placed that the hot junction of the couple was approximately in the longitudinal center of the hot zone and about one-half inch above the axis of the tube. In this position the distance of the sample from the couple was always between one-quarter and one-half inch, the center of the sample being directly under the hot junction of the couple. The thermocouples used were platinum, platinum-rhodium and the voltage they developed was measured by a portable potentiometer graduated in tenths of a millivolt. The porcelain tube was protected from direct contact with the flame of the burners by a D-shaped carborundum muffle. To secure a uniform flow of gas in the tube, it was packed for a distance of about nine inches ahead of the inlet with porcelain chips.

Flowmeters of the ordinary friction type using mercury as the indicating fluid were used for the measurement of quantity in the

case of the permanent gases, carbon dioxide, carbon monoxide, hydrogen, air and commercial illuminating gas. These meters were calibrated in terms of cubic feet per hour against a Sargent wet test meter for the specific gas to be used.

Steam for use in these runs was generated in a small boiler made of 4-inch steel pipe which contained an electric immersion heater. In addition, a smaller boiler was used for low rates of flow since the control of the large boiler was not sufficiently accurate for small outputs. It was necessary to free the steam from any gases dissolved in the water. This was done in each of the boilers by allowing the water to boil vigorously for at least one-half hour and exhausting the steam to the air before connecting the furnace tube.

To introduce steam into a hydrogen stream, a saturator was assembled which consisted of five bottles, connected in series by glass tubing and well sealed. These were immersed in a water bath which could be maintained at constant temperatures within $\pm$ 0.1 degree Cent. The saturator was checked at various points in the range where it was to be used and was found to be accurate within 0.1 per cent. The gas to which water vapor was to be added was always passed through the saturator for about an hour before starting a series of experiments in order to eliminate gases which might have been dissolved in the distilled water used in the bubbling towers.

Carbon monoxide for use in the runs to determine the extension of the Fe: FeO: CO: CO_2 equilibrium was prepared by allowing formic acid to drop slowly into hot concentrated sulphuric acid. Carbon dioxide and hydrogen were obtained from tanks. All of these gases were purified by passing through absorption trains. For gas-air combustion atmospheres, air was taken from the laboratory line and gas from a pressure storage tank which had been filled from the city mains. This insured a source of gas having a constant composition.

The metals used are listed in Table I. The steel samples were prepared for use in 2-inch lengths and polished to a uniform brightness with 00 emery cloth. The electrolytic iron used was in the form of hollow cylinders having a $\frac{1}{32}$-inch wall. These were polished in a manner similar to that of the steel samples.

Method

The procedure used in the scaling tests has been previously

Table I
Chemical Composition of Steels

Steel	Per Cent C	Mn	Si	S	P	Ni	Cr	Va	Mo	W
Electrolytic Iron	0.012	0.008	0.001	0.007	0.002					
1015	0.19	0.53	0.18	0.020	0.016					
1030	0.28	0.653	0.01	0.032	0.013					
1050	0.52	0.64		0.034	0.025					
1090	0.88	0.34		0.018	0.029					
High Carbon Tool Steel	1.12	0.33	0.21	0.026	0.011					
2320	0.17	0.59	0.24	0.020	0.018	3.40				
3130	0.35	0.56		0.025	0.016	1.11	0.56			
6145	0.47	0.58	0.16	0.015	0.015		0.98	0.24		
4140	0.39	0.67		0.024	0.020		0.93		0.32	
4615	0.21	0.54	0.29	0.012	0.017	1.81			0.25	
High Speed Steel	0.73	0.32	0.08	0.018	0.025		4.27	1.06		18.62

described.[26] This procedure was also used in equilibria determinations with hydrogen, steam, and carbon monoxide–carbon dioxide atmospheres. A weighed electrolytic iron cylinder previously described was mounted in the same fashion as the steel samples in the scaling tests and then introduced into the porcelain tube. The atmosphere in the tube had previously been adjusted to the desired ratio of steam to hydrogen or of carbon dioxide to carbon monoxide, and the sample was then exposed to the action of this moving atmosphere for a period of 30 minutes in the case of the steam-hydrogen experiments or for a period of one hour in the case of the carbon dioxide-carbon monoxide determinations. After this exposure the sample was withdrawn into a quenching bath of distilled water as described. The quenching, while it immediately stopped any scaling reaction at high temperatures, resulted in the formation of small amounts of oxide by reaction of the iron with water, particularly on samples which were unscaled in the chosen furnace atmosphere. But the amounts of oxide formed during the short quenching times on unscaled iron or steel were found to be approximately constant for any given temperature at which the metal was immersed.

In the case of steam-hydrogen runs, visual observation served to determine whether or not the sample had scaled in the chosen atmosphere, since the reaction, if it proceeded, gave an easily recognizable quantity of scale. This observation was subsequently checked by determining the loss in weight using the stripping methods outlined in the previous paper. Because the reaction was much slower when

[26] W. E. Jominy and D. W. Murphy, TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 19.

atmospheres of carbon dioxide and carbon monoxide were used, it was necessary when using these atmospheres to rely on weight determinations to ascertain whether the action of the atmosphere had been scaling or non-scaling. The composition of the gases flowing through the tube was then varied until two compositions were found whose contents of oxidizing gas differed by not more than 2 per cent when, at the same temperature, one produced scaling and the other did not. In some cases the difference between the contents of oxidizing gas in two atmospheres was as low as 0.5 per cent, but this small range was not the rule. In the preliminary experiments with carbon dioxide-carbon monoxide mixtures, the usual range between carbon dioxide contents of scaling and non-scaling mixtures was 2 per cent, but in the final experiments this range was decreased to 0.6 per cent. The differentiation between scaled and non-scaled samples was very sharp even with this reduced range, and the method is, consequently, thought to be very sensitive. Fig. 5 is a typical illustration of the data secured and shows the marked increase in oxidation which occurs when the atmosphere becomes slightly oxidizing. At temperatures of 1370 and 1425 degrees Cent. (2500-2600 degrees Fahr.) where the oxide is liquid, it was necessary to alter the method of mounting these samples. Boats were fabricated from a chromium oxide cement to contain two sillimanite crossbars. The boat was brought to the temperature of the furnace and the sample then placed on the two sillimanite bars. At the termination of the run it was only necessary to remove the sample, since one boat was sufficient for several heats. The rest of the procedure at these temperatures was entirely similar to that at lower temperatures.

Gas analyses were necessary to check the condition of the tube, and composition of gas mixtures. The apparatus was a modified Orsat which had provision for the determination of carbon dioxide, oxygen, carbon monoxide, hydrogen, unsaturated hydrocarbons, and hydrocarbons of the methane series.

The total error that may be expected in individual measurements of scaling appeared to be about $\pm$ 2.5 per cent which would indicate a possible variation of 5 per cent between individual runs under like conditions. In the case of determinations of the equilibria in the Fe:O:H and Fe:C:O systems, the only matter of interest was the question of whether or not the sample had scaled. The results were therefore not sensitive to time errors nor to some of the weight errors, since the question of rate of oxidation was not involved. The

chief errors then are those of temperature measurement and gas composition. It has been estimated that the temperature errors may be ± 0.5 per cent while the composition errors may be ± 0.2 per cent, making a total error of ± 0.7 per cent in each determination. The sources of uncertainty in drawing curves will also be reviewed.

Discussion of Results

The variables in the process of the oxidation of iron are the effect of variation of velocity of the gas stream, the effect of variation of the temperature at which the steel is exposed, the effect of varia-

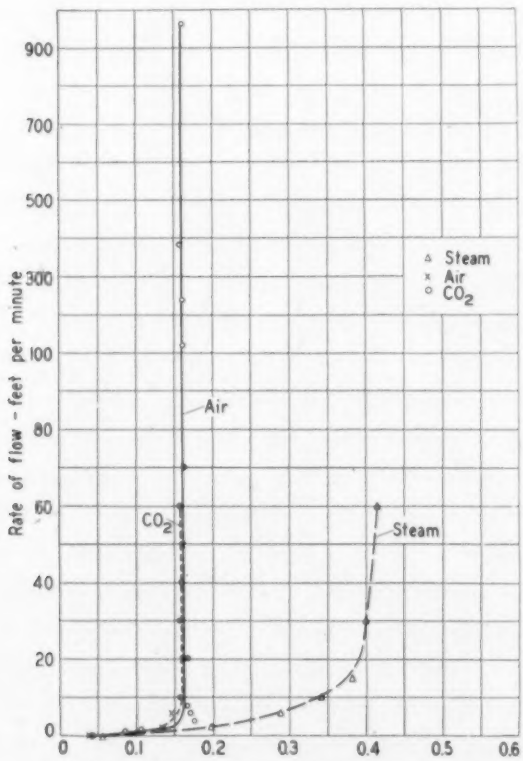

Fig. 1—Effect of Variation of Velocity of Gas on the Scaling of S.A.E. 1015 Steel at 1250 Degrees Cent. (2280 Degrees Fahr.).

tion of time of exposure, the effect of variation of the carbon content of the steel, and the effect of variation of size. The data on variation of time, temperature, and velocity in atmospheres of dry air, carbon dioxide, and steam were presented in a paper by W. E. Jominy and D. W. Murphy[26], previously referred to. These data are reproduced in the curves of Figs. 1, 2, and 3. No discussion of scaling would be complete without reference to the effect of atmosphere. However,

the study of this effect is exceedingly difficult when the products of combustion of city gas and air are chosen as the atmosphere. It will be shown that this problem is considerably simplified by the application of data obtained in the study of equilibria in the systems Fe: FeO: CO: CO_2 and Fe: FeO: H_2 and H_2O. The investigation of these systems at temperatures over 1000 degrees Cent. (1830 degrees Fahr.) has led to some interesting and important information con-

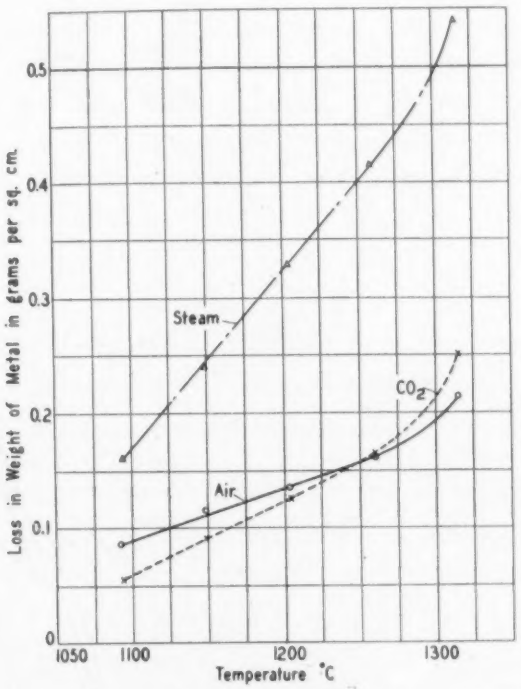

Fig. 2—Effect of Variation of Temperature on the Scaling of S.A.E. 1015 Steel in Various Gases.

nected with the melting of ferrous oxide. The data for the Fe: FeO: H_2: H_2O system was presented in a recent paper by Jominy and Murphy[27] and Figs. 6 and 8 are reproductions of that data.

Effect of Area

The data of Table II show quite conclusively that the oxidation process is a surface phenomenon as it is quite evident that the scaling loss is proportional to the area of the sample. However, there must be a limiting size of sample below which the mass of metal will enter as a factor. This arises from the fact that the reaction in question,

[27] Jominy and Murphy, *Journal of Industrial and Engineering Chemistry*, Vol. 23, 1931, p. 384.

$3Fe + 2\,O_2 \rightarrow Fe_3O_4$, is exothermic. Hence, there will be a tendency as the size of the sample is decreased for the development of heat to increase the temperature of the sample, and, consequently, to increase the rate of reaction. In all cases, however, where the heat resulting from the surface reaction is not concentrated on a relatively small mass, the reaction will proceed as a strictly surface phenomenon, and the amount of metal lost by oxidation will be proportional to the area of the sample. The limiting size, below which the loss of metal by oxidation would cease to be proportional to the area, is not definitely known, and, furthermore, it would vary for different temperatures inasmuch as the concentration of heat is partly dependent on the initial reaction rate. The fact that the scaling loss is proportional to the area offers no clue to the mechanism since it means only that the active mass of iron concerned in the reaction is solely in the surface layer.

Effect of Carbon Content

It is apparent from a consideration of the data presented in Table III and Fig. 4 that the effect of the carbon content of the steel

Table II
Effect of Variation of the Size of Sample on Scaling of SAE 1015 Steel in Dry Air at 1260 Degrees Cent.

Sample Number	Total Time in Furnace, Minutes	Rate of Flow Feet per Minute	Diameter of Sample in Inches	Per Cent Loss in Weight	Loss in Grams per sq. cm.	Wt. of Scale in Grams per sq. cm.	Av. Loss in Wt. / Av. Wt. of Scale
AR7	40	60.0	0.500	7.96	0.1753	0.2428	
AR8	40	60.0	0.500	7.58	0.1672	0.2366	
Average				7.77	0.1712	0.2397	0.715
AR9	40	60.0	0.375	9.65	0.1647	0.2400	
AR10	40	60.0	0.375	9.99	0.1753		
Average				9.82	0.1700	0.2400	0.709
AR11	40	60.0	0.6197	6.86	0.1829	0.2554	
AR12	40	60.0	0.6230	6.66	0.1787	0.2480	
Average				6.76	0.1808	0.2517	0.719
630	40	60.0	0.8138	4.88	0.1675	0.2320	
646	40	60.0	0.8135	5.18	0.1728	0.2406	
Average				5.03	0.1701	0.2363	0.720

is rather capricious at 0.5 per cent and below. It will be noted that the loss of metal by scaling is definitely decreased in the high carbon range. Scott[14] has attributed this to the preferential oxidation of carbon. There is also another possibility which would account for the decreased scaling loss in dry air in the high carbon steels. It

would be expected that the carbon of the steel would be oxidized to carbon monoxide which being present within the scale would have a tendency to retard the oxidizing action. An examination of the ratio column of this table shows that the proportion of FeO in the scale is increasing as the carbon content increases; that is the ratio begins to deviate from 0.724 for Fe_3O_4 toward 0.777 for FeO. This could occur only if the oxidation of FeO to Fe_3O_4 was partially prevented by carbon monoxide. Hence, as the carbon content of the steel increased, the magnitude of the opposing tendency also increased with the net result that the speed of reaction was decreased. In general

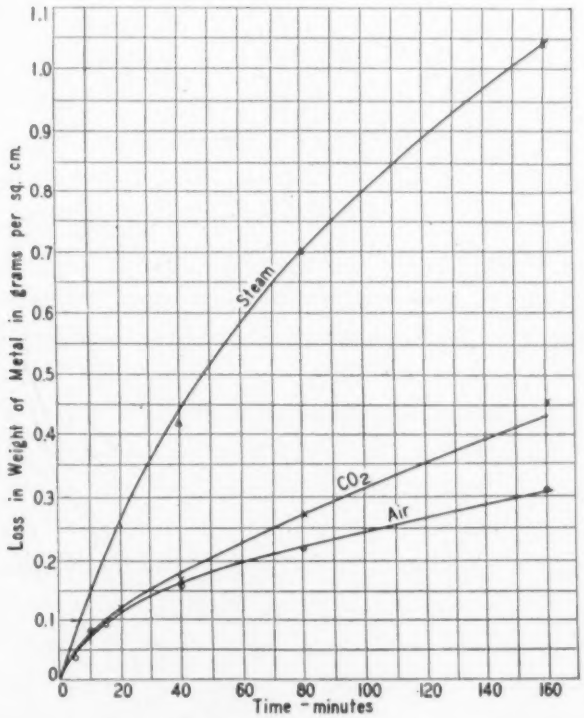

Fig.3—Effect of Variation of Time Exposure on the Scaling of S.A.E. 1015 Steel at 1260 Degrees Cent. (2300 Degrees Fahr.).

this is the effect noted, although the operation of this factor is certainly not pronounced in low carbon steels.

Effect of Velocity

One of the most interesting features of the data shown in Fig. 1, in which the velocity of various gases was varied, is that as the velocity of the stream is increased a constant loss is attained which

Table III
Effect of Variation of Carbon Content on the Scaling of Steel at 1260 Degrees Cent. in Dry Air.

Run No.	Steel	Per Cent Carbon	Velocity of Air Ft. per Minute	Time Minutes	Loss in Weight Per Cent	Loss in Weight Gms. per sq. cm.	Weight of Scale Gms. per sq. cm.	Ratio Loss in Wgt. Wgt. of Scale
338	1015	0.18	60	40	4.86	0.1640		
630	1015	0.18	60	40	4.88	0.1675	0.2320	0.723
avg.					4.87	0.1657		
A1-21	1030	0.28	60	40	8.09	0.2485	0.3520	
A1-22	1030	0.28	60	40	7.91	0.2455	0.3420	
avg.					8.00	0.2470	0.3470	0.712
A2-18	1050	0.52	60	40	7.35	0.2320	0.3240	
A2-19	1050	0.52	60	40	6.65	0.2100	0.2840	
avg.					7.00	0.2210	0.3040	0.727
A3-17	1090	0.88	60	40	6.35	0.2000	0.2720	
A3-18	1090	0.88	60	40	6.30	0.1980	0.2700	
avg.					6.33	0.1990	0.2710	0.735
E-18	High C	1.12	60	40	4.99	0.1790	0.2395	
E-19	High C	1.12	60	40	4.62	0.1652	0.2200	
avg.					4.80	0.1721	0.2298	0.750

does not appear to be affected by a further increase in velocity. There is no probable mechanism of continued oxidation of a metallic surface which does not include migration of oxygen inward through the scale after the first oxidation has occurred. If no such transfer of oxygen were present, the process of oxidation would be considerably inhibited since it could only take place upon iron which had diffused outward provided the scale remained intact on the surface. Even the various theories in which higher oxides are regarded as oxygen carriers in reality reduce to a diffusion phenomenon for in this case the inward diffusion of oxygen is accomplished by the alternate formation and reduction of higher oxides. Since any plausible mechanism must provide for diffusion of the oxidizing agent through the scale, the question of supply of the oxidizing agent must occur. Admittedly, the supply of oxygen is dependent on the velocity of the gas stream which must replenish the oxidizing agent absorbed by the reaction from the film of gas surrounding the metallic sample. From this reasoning it appears that rates of flow of gas must exist which cannot maintain the supply of oxidizing agent at a sufficient level to satisfy the requirements of the reaction at the particular temperature being studied. Likewise, it is evident that when the rate of supply becomes equal to the maximum rate at which the oxidizing agent is used at the temperature in question, the reaction proceeds to its full extent and no further increase in rate of supply can alter the amount of metal entering the oxidizing reaction. The characteristics of the curves of Fig. 1 evidently fulfill this conception. First, then, to

secure comparable results on rates of oxidation, it is necessary to carry on the experiments in a range of velocity where the supply of the oxidizing agent is assuredly more than equivalent to the rate at which this agent can be used. For this reason observations of scaling

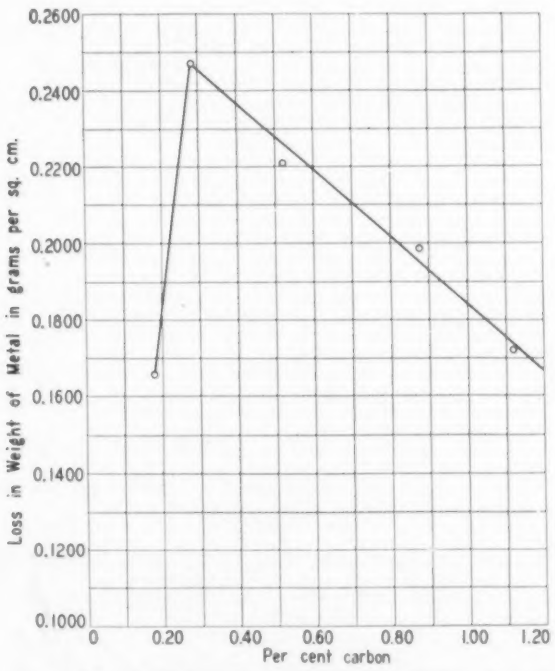

Fig. 4—Effect of Variation of Carbon Content of Steel on the Scaling in Dry Air at 1260 Degrees Cent. (2300 Degrees Fahr.).

rates in this work have been carried on with rates of flow of 60 feet per minute, a rate which seems to insure ample supply.

Effect of Temperature

Temperature, of course, has a pronounced effect on the rate of oxidation of steel, as is clearly demonstrated in Fig. 2. The curves in the region covered in this research seem to be nearly linear until the melting point of the oxide is attained. The sharp break which occurs in all the curves above 1315 degrees Cent. is additional evidence that the degree of continued oxidation is conditioned upon the protective action of the scale. Since the melting point of the oxide scale lies below 1370 degrees Cent. (2500 degrees Fahr.) the scale must exist in a molten condition at this latter temperature, and in the molten state its protective action against further oxidation is destroyed. The empirical expressions for the curves of Fig. 2 are easily

established for the range 1095 to 1315 degrees Cent. (2000-2400 degrees Fahr.) according to the general form $W = A + BT$, where W is the loss in weight in grams per square centimeter for 40 minute runs, T is the temperature in degrees Centigrade, and A and B are constants. For the three gases dry air, steam, and carbon dioxide, the data from 1095 to 1315 degrees Cent. (2000-2400 degrees Fahr.) may be expressed as follows: for air $W = 0.000455T - 0.4118$; for steam, $W = 0.001539T - 1.5244$; and for carbon dioxide, $W = 0.000638T - 0.6375$.

Effect of Time

From the form of the curves of Fig. 3 where loss in weight per square centimeter is plotted against time, it is apparent that the rate of oxidation is diminished as time is increased. Since the mechanism must involve diffusion of the oxidizing gas through an increasing thickness of scale, it is evident that this diffusion factor will operate to reduce the rate of oxidation as the time of exposure increases. For air the data for 1260 degrees Cent. (2300 degrees Fahr.) yield the equation $W^2 = 0.000604t$, where W is the loss in weight per unit of area, and t is the total time in the furnace in minutes.

The data with steam and carbon dioxide are not so easily reduced to empirical formulae. The results with steam are well expressed by an equation of the type $W^2 = kt + b$. This type is bound to fail for short times because of the constant "b". Evaluation of the constants yields the expression: $W^2 = 0.007371\ t - 0.0986$. It is evident that with this type of equation representing the data at 1260 degrees Cent. there is insufficient data in Table VI to permit a calculation of the reaction constants at the various temperatures. The data for carbon dioxide are best expressed by the equation $t = (26.86\ W + 1.605)^2$. To determine the weight, — time, — temperature equation would in this case, also, require more data than that presented in Fig. 2. The rate of oxidation unquestionably falls off as time increases.

The Mechanism of Oxidation

Pfeil[25] in his excellent research established the fact that oxides of high oxygen content will react with oxides of lower oxygen content even when the oxides are not actually in contact. But this reaction is without doubt slow according to the time periods used to establish the trend of the reaction, and, consequently, no great amount

of oxidation would result by this means. But his chief addition to the theory of the mechanism of scaling was that in addition to the oxygen diffusing inward through the scale, the iron must also diffuse outward through the scale.

In support of his theory that iron must also diffuse outward, Pfeil cited several phenomena, among the most interesting of which was the occurrence of punch markings within the body of the scale. These markings originally present on the surface of the steel were

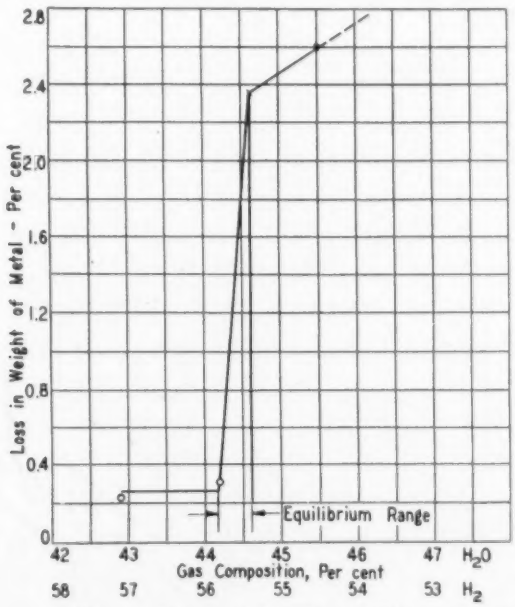

Fig. 5—Effect of Small Variations of Gas Composition Near the True Equilibrium Range on the Loss in Weight of Iron Samples at 1260 Degrees Cent. (2300 Degrees Fahr.). Data from Fe-O-H System.

preserved in relief in their original outline at a position which corresponded with the initial dimensions of the steel sample. The relief figures were evident in the middle portion of the scale and accordingly were not visible on the outside or the inside when the scaling process had been carried on for a sufficient length of time to diminish considerably the dimensions of the sample. The fact that the figures were built in relief and were imbedded in scale at their original position could only be explained by the outward diffusion of iron. Obviously any plastic flow in the scale would cause at least a distortion, if not a total disappearance, of any figures arising from the original configurations on the surface of the steel. This phenomenon cited by Pfeil has been confirmed in the present work.

The mechanism of solid diffusion seems to involve the assumption that the diffusing solid shall first dissolve in the solid through which it must diffuse. The driving force for diffusion must then depend on a difference in concentration of the diffusing solid between that portion of the solid solution which is in immediate contact with the diffusing solid, and which may be considered as saturated with respect to that solid and the main portion of the solid solution. Thus, if there were no possibility of maintaining the main portion of the solid solution in an unsaturated state with respect to the diffusing solid, the diffusion would cease when the whole portion of the solid solution had become saturated. The oxidizing power of a certain gas would then be partly conditioned on the ease with which it would maintain the main portion of the oxide scale in an unsaturated condition with respect to iron; and this in turn is dependent on the speed with which the gas molecules can diffuse into or permeate the main portion of the oxide. Of course, the maintenance of a continuous diffusion of iron outward would also necessitate at all times an oxide-metal interface, since, if this interface was destroyed, no iron could be withdrawn from the main body of the metal except as vapor which would be highly improbable at the temperatures involved.

The results obtained with carbon dioxide and steam yield interesting information concerning the nature of the process of oxidation which has been briefly postulated. If the scaling losses at 1260 degrees Cent. for various times in an atmosphere of steam are divided by the scaling losses at the same temperature for the corresponding times in an atmosphere of carbon dioxide, it will be observed that the ratio of losses in the two atmospheres is approximately constant having a value of 2.5. The rates of these two reactions, of iron with steam, and of iron with carbon dioxide, must be proportional to the relative speeds of diffusion of the individual gases, to the effective driving force which enables diffusion to proceed and, according to Pfeil, to the rate of diffusion of iron. According to Graham's law of diffusion, the amount of gas diffusing through the scale is expressed as follows: $D \propto \sqrt{\frac{1}{M}} \triangle \rho$

where M is the molecular weight of the diffusing gas and $\triangle \rho$ is the effective driving force causing diffusion. The loss in weight, W, will of course, be directly proportional to the amount of oxidizing gas diffusing inward and also to the amount of reducing gas diffusing

outward and hence the loss in weight will be proportional to the product of the amounts of gases diffusing. The term $\triangle\rho$ is considered as the difference in concentration of the diffusing gas at the outside of the scale and its concentration at some point within the scale where equilibrium may be considered to have been established. The equilibrium concentrations of carbon dioxide and carbon monoxide and of steam and hydrogen in contact with iron and ferrous oxide are given in Figs. 6 and 7. The driving force at 1260 degrees Cent. for the inward diffusion of carbon dioxide is 1.00 — 0.22 or 0.78 since the gas outside the scale is pure carbon dioxide and since at the point where equilibrium is assumed, the concentration of carbon dioxide is 22 per cent or 0.22 mol fraction as read from Fig. 7. Likewise the driving force for the outward diffusion of carbon monoxide is 0.78 —0 or 0.78 since its concentration at the equilibrium point is 78 per cent or 0.78 mol fraction while in the atmosphere outside the scale its concentration is not greatly different from 0.

From this reasoning, omitting for the present any discussion of the diffusion of iron, the gaseous diffusion factors affecting loss in weight by scaling in carbon dioxide atmospheres may be formulated as follows: $W \propto \sqrt{\frac{1}{CO_2}} \triangle p_{co_2} \sqrt{\frac{1}{CO}} \triangle p_{co}$ where W is the loss in weight and CO and CO_2 represent the molecular weights of these gases. In this expression the relative speeds of diffusion of gaseous reagent and product and the driving force available to cause diffusion in each case occur. In a like manner the reaction with steam may be formulated as $W \propto \sqrt{\frac{1}{H_2}} \triangle p_{H_2} \sqrt{\frac{1}{H_2O}} \triangle p_{H_2O}$. The expression for oxidation in carbon dioxide atmospheres becomes $W \propto \sqrt{\frac{1}{44}} \times 0.78 \times \sqrt{\frac{1}{28}} \times 0.78$ when the molecular weights and the proper values of $\triangle p_{co_2}$ and $\triangle p_{co}$ are substituted. When the indicated operations are performed $W \propto 0.0173$ at 1260 degrees Cent. for carbon dioxide oxidation. In the case of steam the expression $W \propto \frac{1}{H_2} \times p_{H_2} \sqrt{\frac{1}{H_2O}} p_{H_2O}$ becomes $W \propto \sqrt{\frac{1}{2}} \times 0.56 \times \sqrt{\frac{1}{18}} \times 0.56$ or $W \propto 0.0524$. On this basis it would appear that

the scaling losses in steam and carbon dioxide atmospheres should possess the ratio $\frac{0.0524}{0.0173}$ at 1260 degrees Cent. or 3.02. Actually it was found that this ratio has a value of 2.5 which is somewhat lower than the calculated value indicating that the scaling in carbon dioxide was more vigorous than the previous calculation would indicate.

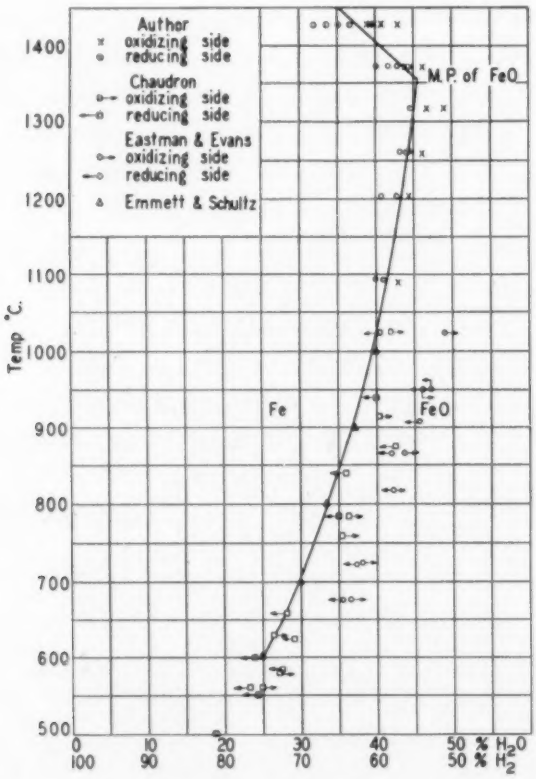

Fig. 6—Equilibrium Compositions for the System Fe-FeO-H_2-H_2O.

Pfeil has suggested that the rate of scaling also depends on the rate of diffusion of iron outward through the scale. Thus far in the discussion only the diffusion of the gaseous reagents and products have been considered and it is seen that this does not lead to a complete correlation of the two sets of data. In order to account for the lower observed ratio of scaling losses in the two gases it will be necessary to introduce this third factor, namely the diffusion of iron. It then appears probable that the effective rate of diffusion of iron through the scale instead of being equal in the two cases as was tacitly assumed in the previous formulation is somewhat greater in the case of oxi-

dation with carbon dioxide than in the case of oxidation with steam. In fact it would be expected that the effective rates of diffusion of iron through oxides formed by carbon dioxide and in steam would be in the ratio of $\frac{3.0}{2.5}$ where 3.0 is the calculated ratio of loss in weight in steam to loss in weight in carbon dioxide and 2.5 is the observed ratio of losses. The effective rate of diffusion of iron in the case of oxidation by carbon dioxide would thus be 1.2 times the effective

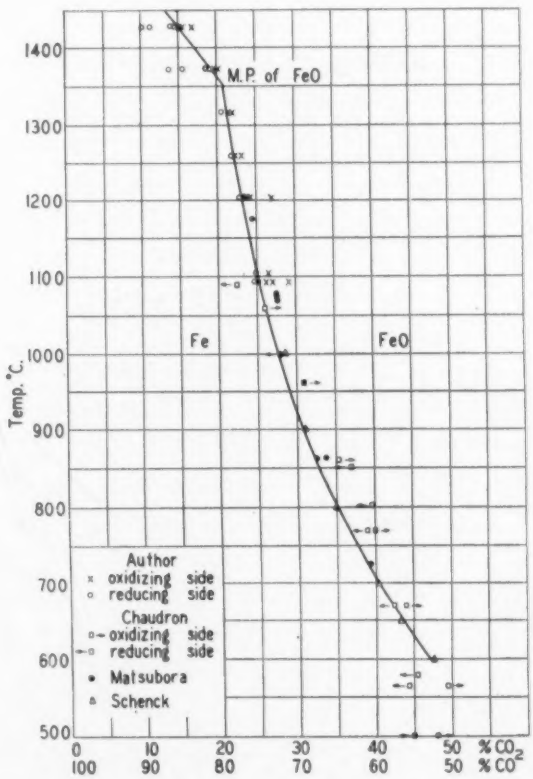

Fig. 7—Equilibrium Compositions for the System Fe-FeO: CO-CO_2.

rate of diffusion of iron in the case of oxidation with steam. It has been consistently observed in this research that the scale formed in carbon dioxide atmospheres adheres more tenaciously to the steel than does that formed in steam atmospheres. The tenacity of adherence of the scale to steel is at least partly dependent on the porosity of the scale so that the carbon dioxide scales would be somewhat less porous than the steam scales. This slight difference in porosity would allow for a slightly greater effective rate of diffusion of iron through

the carbon dioxide scale than through the steam scale since the area available for diffusion is greater in the carbon dioxide scales.

From the foregoing reasoning the effect of the diffusional properties of the gas is apparent. Since the diffusion of steam through the scale according to Graham's law will be more rapid than that of carbon dioxide, the oxide layers in the case of oxidation under water vapor atmospheres will be more easily maintained in a state of unsaturation with respect to iron than in the case of carbon dioxide oxidation. This will allow a greater diffusion of iron and consequently a more rapid growth of the oxide layers. In addition, the gaseous product of oxidation of iron with steam possesses a more rapid rate of diffusion than does the gaseous product of oxidation with carbon dioxide, so that the presence of hydrogen in the first case will retard the reaction to a lesser degree than will the presence of carbon monoxide in the second case. It is evident, then, that the diffusion of reagent and product will operate so that the reaction with steam may proceed with considerably greater speed than that reaction with carbon dioxide.

The mechanism as now conceived involves the molecular diffusion of oxidizing gas inward and a diffusion of iron outward. The magnitude of the scaling effect at a given temperature during any time is at least partly dependent upon the relative speeds of diffusion of gaseous reagent and product. The magnitude of the effect is also dependent on the rate of diffusion of iron outward, which has been postulated as being affected by the relative speeds of diffusion of gaseous product and reagent considering that the diffusion rate is dependent upon the ease with which the main portion of the scale is maintained in a state of unsaturation with respect to iron. The speeds of diffusion of gaseous reagent and product may also affect the maintenance of a metal oxide interface and thus the rate of oxidation.

X-Ray Studies of Oxides

The similarity of the scales produced in carbon dioxide and steam is borne out by examination of the data derived from X-ray studies and summarized in Table IV which shows that there is no variation of lattice constant of either FeO or Fe_3O_4 with temperature or atmosphere. Wykoff[28] has given 4.29 Angstrom units as the constant of FeO, and 8.37 Angstrom units as the constant of Fe_3O_4.

[28]Wykoff, The Structure of Crystals; Chemical Catalogue Co.

Table IV
Variation of Lattice Constants and Chemical Composition of Oxides with Temperature.

Run No.	Atmosphere	Temperature Degrees Cent.	FeO Lattice Const.	Fe_3O_4 Lattice Const.	% Fe	% FeO	% Fe_3O_4
271	CO_2	1149	4.287	8.379	0.13	61.5	37.7
276	CO_2	1206	4.287		0.19	60.3	38.7
451	CO_2	1260	4.287	8.379	0.13	59.0	39.6
521	CO_2	1316	4.287		0.10	60.4	38.5
548	CO_2	1371	4.286	8.379			
236	H_2O	1093	4.288	8.374	0.10	62.9	35.0
237	H_2O	1149	4.288		0.18	66.0	31.8
240	H_2O	1206	4.288	8.371	0.19	63.5	35.3
499	H_2O	1260	4.286	8.375	0.10	64.3	33.8
267	H_2O	1316	4.287		0.13	61.1	36.6
	H_2O-H_2	1260	4.289				
	H_2O-H_2	1427	4.289				

Two oxides whose constants are of similar magnitude are shown to exist, one having a constant of 4.288Å and the other having a constant of 8.375Å. These may be identified as FeO and Fe_3O_4 by comparison with Wykoff's values. X-rays failed to reveal any distinct metallic iron lattice in these oxides. There seems to be no distortion of the FeO lattice so that the quantity of iron in solution in the oxide may be assumed to be very small. Chemical analysis has indicated the presence of 0.1 to 0.2 per cent metallic iron. Two samples of oxide which were produced with a slightly oxidizing mixture of hydrogen and steam, one at a temperature below the melting point and the other at a temperature above the melting point, were photographed by means of X-rays. In the preparation of these two samples of oxide the atmospheres were so adjusted that no free ferro-ferric oxide could result from oxidation in the furnace since the mixtures of hydrogen and steam were only slightly oxidizing with respect to iron. Consequently, these samples should consist of nearly pure ferrous oxide since both were cooled extremely rapidly from the temperature of formation. It is possible then to place considerable reliance on the constant determined from these two samples of oxide which is 4.289Å. This is in good agreement with the value given by Wykoff and cited previously. It has been mentioned that the lattice constants of FeO as given in Table IV show no variation with respect to temperature and atmosphere. It does not seem conceivable that large quantities of ferro-ferric oxide could dissolve in ferrous oxide without a considerable lattice distortion in view of the marked difference in lattice constants of the two oxides. From these facts there appears to be small possibility of extensive solid solution of ferro-ferric oxide or iron in ferrous oxide.

There has in the past been some idea that ferrous oxide lost its identity above the melting point. One sample of scale formed under an atmosphere of carbon dioxide at 1370 degrees Cent. (2500 degrees Fahr.) which is definitely above the melting point, and another sample obtained at 1425 degrees Cent. (2600 degrees Fahr.) with an atmosphere of hydrogen and water vapor so adjusted as to be slightly

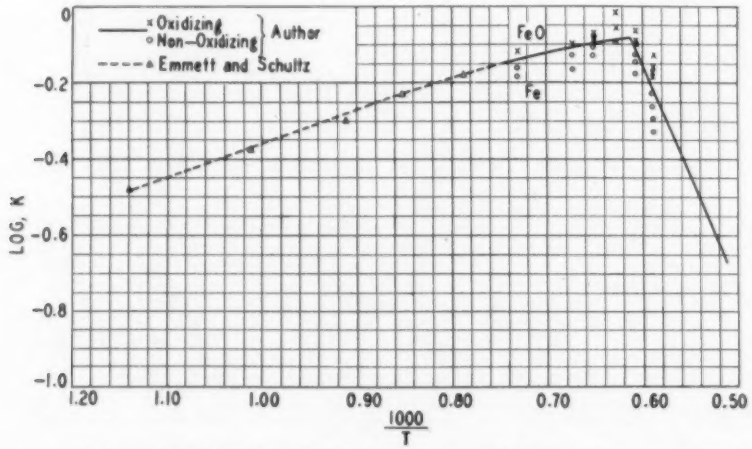

Fig. 8—Equilibrium Constants on the Fe-O-H System at Temperatures up to 1425 Degrees Cent. (2600 Degrees Fahr.).

oxidizing, were subjected to X-ray analysis. The results appear in Table IV. When the values of the constants of these two samples are compared with those formed below 1370 degrees Cent. (2500 degrees Fahr.) there can be no doubt that the lattice constant of ferrous oxide has undergone no alteration by reason of having been formed in the molten state. It, therefore, seems reasonable to assert that ferrous oxide is stable above its melting point. This point is of interest in view of the equilibrium data obtained in this work.

Equilibria in the Systems Fe:O:H and Fe:O:C

During the course of the investigation it appeared that the methods which had been developed for the determination of rates of scaling could also be applied to the extension of the data on the systems Fe: FeO: H_2: H_2O and Fe: FeO: CO: CO_2 to higher temperatures than had previously been used. The basis of the adaptation of the scaling methods to equilibrium determinations is that at any temperature the true composition of a gaseous phase in equilibrium with a solid phase consisting of Fe and FeO must lie between two gas phase compositions of which one produces oxidation of iron

and the other does not. If the gas phase has a sufficient velocity, the effect of each type of atmosphere on iron may be ascertained without reference to the composition of the gases after contact with the sample. An atmosphere which contains slightly more than the necessary amount of reducing agent required to prevent scaling will of course result in no oxidation, while an atmosphere that contains slightly less than the necessary amount will cause oxidation. The com-

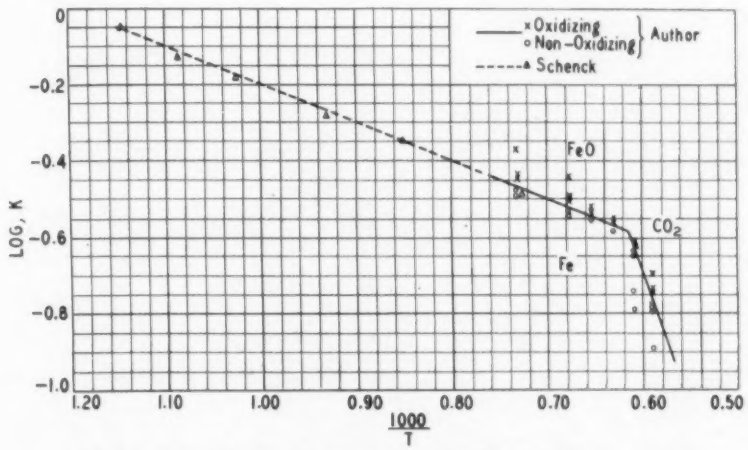

Fig. 9—Equilibrium Constants on the Fe-C-O System at Temperatures up to 1427 Degrees Cent. (2600 Degrees Fahr.).

plete curve is drawn, as shown in Figs. 6, 7, 8, and 9, so that at all temperatures it lies within the narrowest range between oxidizing and non-oxidizing compositions of the atmosphere. The range of composition between oxidizing and non-oxidizing atmospheres, may, of course, be within any desired limits. It must be remembered, however, that the narrower the range, the more time will be necessary to establish the effect of any certain atmosphere on iron since the rate of oxidation as the true equilibrium composition is approached becomes very slow.

It is apparent from Figs. 6 and 7 in which the gas composition is plotted against temperature in degrees Centigrade, that the data for these two systems furnish an excellent check on the work of Emmett and Schultz[10] in the Fe:O:H system and on the researches of Schenck[13] in the Fe:O:C system. For comparison with the work of other authors the results of some researches have been plotted. It will be observed that Eastman and Evans'[3] data on the Fe:O:H systems, which it may be said agree generally with that of Schreiner and Grimnes[29] and that of Wohler,[30] are definitely in the oxide region

Table V

Scaling and Non-scaling Mixtures of Carbon Dioxide and Carbon Monoxide at Temperatures of 1095 to 1425 Degrees Cent.

Run No.	Temperature Degrees Cent.	Per Cent CO_2	Condition of Sample After Testing	Equil. Const. $K=\frac{PCO_2}{PCO}$	$-\text{Log } K$
54	1093	29.2	Scaled	0.413	0.384
34	1093	27.0	Scaled	0.370	0.432
33	1093	26.9	Scaled	0.368	0.434
35	1093	26.4	Scaled	0.358	0.446
59	1093	25.3	Not Scaled	0.339	0.470
60	1093	24.8	Not Scaled	0.330	0.481
44	1102	26.5		0.360	0.444
56	1104	25.0		0.333	0.477
38	1204	27.0	Scaled	0.370	0.432
36	1204	24.3	Scaled	0.321	0.493
39	1204	23.7	Scaled	0.311	0.507
62	1204	23.6	Scaled	0.309	0.510
37	1204	22.9	Not Scaled	0.297	0.527
66	1204	22.8	Not Scaled	0.295	0.530
40	1260	23.2	Scaled	0.302	0.520
64	1260	22.4	Scaled	0.289	0.539
41	1260	22.0	Not Scaled	0.282	0.550
65	1260	22.0	Not Scaled	0.282	0.550
43	1316	22.0	Scaled	0.282	0.550
50	1316	21.4	Scaled	0.272	0.565
42	1316	20.6	Not Scaled	0.260	0.585
52	1371	20.0	Scaled	0.250	0.602
68	1371	19.6	Scaled	0.244	0.613
67	1371	19.1	Not Scaled	0.236	0.627
51	1371	18.7	Not Scaled	0.230	0.638
46	1371	15.5	Not Scaled	0.183	0.738
47	1371	13.8	Not Scaled	0.160	0.796
53	1427	16.7	Scaled	0.200	0.699
55	1427	15.5	Scaled	0.184	0.735
69	1427	15.1	Scaled	0.178	0.750
70	1427	14.6	Not Scaled	0.171	0.767
58	1427	14.3	Not Scaled	0.167	0.777
71	1427	14.0	Not Scaled	0.163	0.788
48	1427	11.3	Not Scaled	0.121	0.896
49	1427	10.2	Not Scaled	0.114	0.943

according to the data presented in this paper and that presented by Emmett and Schultz. The results of Chaudron[31] which are characteristic of the group of authors who found lower values of the equilibrium constant pH_2O/pH_2 are not so very different from those of Emmett and Schultz. For the Fe:C:O system, the data of Matsubara,[11] of Schenck,[13] and of Chaudron,[32] are plotted in Fig. 7. In general their results are not widely different but our data obtained at high temperatures and shown in Table V are in better agreement with Schenck's latest values, and, hence, his values have been used as the lower extension of the diagram in the Fe:C:O system.

[29]Schreiner and Grimnes, *Zeitschrift fuer Anorganische und Allgemeine Chemie*, Vol. 110, 1920, p. 311.

[30]Wohler, et al., *Zeitschrift fuer Elektrochemie und Angewandte Physikalische Chemie*, Vol. 23, 1917, p. 119; Vol. 27, 1921, p. 406; Vol. 29, 1923, p. 226.

[31]Chaudron, *Comptes Rendus*, Vol. 159, 1914, p. 237; *Ann. chem. phys.*, Vol. 16, 1921, p. 221.

[32]Chaudron, *Comptes Rendus*, Vol. 172, 1921, p. 152.

In the description of methods previously used by investigators of such systems it will be noted that with few exceptions the method employed has been a so-called static one. The principal exceptions are Emmett and Schultz who devised an excellent flow method for the Fe:O:H system, and whose results, it has been observed, furnish an excellent basis for the indirect calculation of water-gas constants. Emmett and Schultz have advanced the hypothesis that certain surface phenomena in the case of the Fe:O:H system gave rise to abnormal or false equilibria in the static methods which were exceedingly difficult to correct. On the basis of the variables which influence the mechanism of oxidation, and which have been discussed, there are possibly two other sources of difficulty in the static methods. One is based on the fact that in these methods the circulation of gas is very slow at the best, and, hence, when any abnormal reaction has occurred at the solid surface, the correction of this condition may be extremely difficult on account of the slowness of the reaction at low velocities; hence, false equilibria would be rendered easy to attain. The other possible difficulty arises from the fact that in this method as applied to the Fe:O:H system low pressures were used which also tended to retard the speed of any reaction which might have begun. Both the velocity and pressure factors operate in such a way that the reaction is rendered slow, probably much more so than many authors believed, so that the attainment of a true equilibrium would require a long time if any reactions had occurred with abnormal intensity at the beginning. Although many investigators have claimed that they have positively approached equilibrium from both directions, a consideration of their results in view of the evident slowness of the reaction under the condition with which they worked renders the truth of this assertion doubtful. Certainly, the conditions of many experiments were such that an abnormal reaction at the start might never be corrected in a reasonable length of time. With the flow methods at atmospheric pressure the reactions are much intensified and their true direction easily ascertained.

The melting point of the oxide is shown as a definite discontinuity at 1360 degrees Cent. in the curves of the composition temperature diagrams in Figs. 6 and 7. For both the Fe:C:O and Fe:H:O systems this discontinuity occurs at nearly the same temperature so there is reason to believe that the discontinuity arises from the same source, the melting of FeO, in both cases. Of course, there

are several possible positions for a line drawn within the range between the oxidizing and non-oxidizing atmospheres at 1370 degrees Cent. and 1425 degrees Cent. (2500-2600 degrees Fahr.) and in each of these positions the line would intersect the curve for solid FeO at a slightly different temperature so that the melting point can be considered as 1360 degrees Cent. ± 5 degrees Cent. (2480 degrees Fahr. ± 9 degrees Fahr.) excluding the inherent errors of temperature measurement which have already been cited. The identity of the oxide both above and below the melting point has already been established on the basis of the X-ray diagrams of this work.

The heat of fusion of ferrous oxide may be calculated from our data. In Figs. 8 and 9 the values of log K have been plotted against 1/T, when K is pH_2O/pH_2 or pCO_2/pCO, and T is degrees absolute. The curves in these figures have likewise been drawn so that at all temperatures they lie within the range between oxidizing and non-oxidizing atmospheres. The thermodynamic formula $\frac{d \ln K}{dT} = \frac{\triangle H}{RT^2}$, where $\triangle H$ is the heat of reaction, and R the universal gas constant, is employed to find the heat of fusion. This may be rewritten,

$$\frac{d \ln K}{\frac{dT}{T^2}} = \frac{\triangle H}{R}, \text{ or } \frac{d \ln K}{d\left(\frac{1}{T}\right)} = \frac{-\triangle H}{R}$$

The heat of reaction then is simply the slope of the $\ln K - \frac{1}{T}$ curve at any point multiplied by R. If the heats of reaction in the direction $FeO + H_2 = Fe + H_2O$ or $FeO + CO \rightleftarrows Fe + CO_2$ are determined at the melting point, one being derived from the curve for solid FeO and the other from the curve for liquid FeO, the difference between these heats of reaction is attributed to the absorption of energy in causing FeO to liquefy. These calculations have accordingly been carried out for both systems and yield the following results:

Fe:H:O below melting point $\triangle H = +2300$ cal/gm mol
Fe:H:O above melting point $\triangle H = -26600$ cal/gm mol
Heat of fusion of FeO = + 28900 cal/gm mol
Fe:C:O below melting point $\triangle H = -4600$ cal/gm mol
Fe:C:O above melting point $\triangle H = -31300$ cal/gm mol
Heat of fusion of FeO = + 26700 cal/gm mol

The values of the heat of fusion check to 2200 cal., the average being +28000 calories per gram mol. However, since the same error is resident in drawing the curves above the melting point, namely the fact that a line drawn within the range between oxidizing and non-oxidizing atmospheres may occupy several positions, this value of +28000 calories can be considered correct only to ±5000 calories. As far as is known these are the only data secured at sufficiently high temperatures to permit a calculation of the heat of fusion.

In summing up previous work C. H. Herty, Jr.[9] has given 1355 to 1370 degrees Cent. (2470-2500 degrees Fahr.) as the melting point of ferrous oxide, and the result previously given based on discontinuities of curves yields 1360 degrees Cent. which is in good agreement with the values presented by Herty.

Scaling in the Products of Combustion of Gas

When city gas and air are burned, the city gas being in excess, carbon dioxide, carbon monoxide, steam and hydrogen are present in the products of combustion. These will adjust themselves in amount to conform to the water-gas constant for the particular temperature. In calculating the water-gas constant indirectly from the Fe:O:H and Fe:C:O systems the ratios H_2O/H_2 and CO_2/CO are combined so that a non-scaling mixture of the four gases will be required to possess certain ratios of H_2O/H_2 and CO_2/CO while an oxidizing mixture will have other values for these ratios. For instance at 1260 degrees Cent. (2300 degrees Fahr.) the ratio of CO_2/CO has a value 0.288, while the ratio H_2O/H_2 has a value of 0.792, both for non-scaling atmospheres. Those atmospheres in which these ratios are greater in value at this temperature than the values just given will produce oxidation.

In Table VI various data are presented for scaling and non-scaling experiments at 1260 degrees Cent. (2300 degrees Fahr.) in atmospheres consisting of the products of combustion of city gas and air. This table shows for a number of steels that atmospheres which yield ratios in excess of those read from the equilibria data of the two systems produce oxidation, while those atmospheres which yield ratios whose value is less than those from the equilibria data produce no oxidation. This apparently holds true for a fairly wide range of steels, but the adjustment of atmosphere has not in most cases been sufficiently close to determine whether or not the equilibria

Table VI
Comparison of CO_2-CO and H_2O-H_2 Ratios for Scaling and Non-scaling Tests on Various Steels at 1260 Degrees Cent. All Runs 40 Minutes.

Run No.	Steel	$K_1 = \frac{PCO_2}{PCO}$	$K_2 = \frac{PH_2O}{PH_2}$	Condition After Testing
A1-19	1030	0.346	0.879	Scaled
A1-20	1030	0.199	0.479	Not Scaled
A2-15	1050	0.346	0.880	Scaled
A2-17	1050	0.199	0.579	Not Scaled
A3-10	1090	0.675	1.85	Scaled
A3-16	1090	0.199	0.479	Not Scaled
E-15	1.12%C	0.333	0.875	Scaled
E-17	1.12%C	0.337	0.310	Not Scaled
FF-14	2320	0.450	1.07	Scaled
FF-15	2320	0.238	0.639	Not Scaled
G-14	3130	0.431	1.07	Scaled
G-16	3130	0.219	0.495	Not Scaled
Q-21	6145	0.420	1.05	Scaled
Q-15	6145	0.238	0.639	Not Scaled
L-11	4615	0.610	1.36	Scaled
L-14	4615	0.304	0.670	Not Scaled
KK-14	4140	0.530	1.47	Scaled
KK-3	4140	0.300	0.520	Not Scaled
YY-13	High Speed	0.354	0.803	Scaled
YY-15	High Speed	0.238	0.639	Not Scaled

Value $\%CO_2/\%CO$ ratio from Figure 7 0.288 at 1260 Degrees Cent.
Value $\%H_2O/\%H_2$ ratio from Figure 6 0.792 at 1260 Degrees Cent.

data can be applied to steels having high alloy contents. It is true, however, that the data on the Fe:H:O and Fe:C:O systems, which have in this research been extended to 1425 degrees Cent. (2600 degrees Fahr.) can be used as a general guide to determine the probable effect of a certain atmosphere on steel at any chosen temperature. It should be remembered, however, that application of these data is conditioned upon the combustion gases attaining equilibrium before the surface of the steel is reached; without this condition obtaining the effect of any atmosphere must necessarily be uncertain.

While most of the variables operative in the oxidation of steel have been discussed here it is appreciated that there are some which have not been touched. Among these are the effect of surface conditions of the steel and the effect of elements other than carbon occurring in the steel as well as the special elements appearing in alloy steels. Further information concerning the rate of diffusion of iron through oxides and the factors affecting this diffusion as well as information regarding the rates of diffusion of various gases through oxides would prove highly interesting. Until such data are available over a considerable temperature range it will not be possible to outline a complete theory regarding the process of oxidation.

Further research in the equilibria of the systems Fe:FeO:H_2:H_2O and Fe:FeO:CO:CO_2 particularly above the melting point

of the oxide and above the temperatures attained in this investigation would aid considerably in establishing more definitely the heat of fusion of the oxide and the phase boundaries.

ACKNOWLEDGMENT

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DISCUSSION

Written Discussion: By Yap, Chu-Phay, physical metallurgist and chemist, 27 Grove St., New York City.

This is an important piece of investigation, apparently well planned and executed, and I wish to congratulate the authors. I predict that this paper will be frequently referred to in the future by theoretical chemists interested in thermodynamics from the standpoint of free energy. In my own study in the free energy of formation of Fe_3C, I found as many sets of experimental data which do not agree with one another as those found by the authors.

The method adopted by them is somewhat similar to the so-called "null" method used by Johansson and von Seth[1] in their study of carburization and decarburization of steel at high temperatures. Because carburization and decarburization can be followed with a microscope and by weighing, Johansson and von Seth were able to approach the equilibrium CO/CO_2 ratio from both sides. This method, I am sure, is not feasible in the case of the problems studied by Messrs. Murphy, Wood and Jominy. Because the closest composition interval of the gases within which the equilibrium point may be defined, was set at 1 per cent, it is unfortunate that they have been unable to give quantitative figures regarding loss in weight in order to enable us to approximate more closely the real equilibrium compositions to within ± 0.2 per cent H_2 or CO. I also wish they had not used a portable potentiometer (manufactured, I presume, by a well-known American firm) because my own experience with this type of potentiometer indicates it is not extremely accurate. Fortunately the gas equilibrium constant K of H_2O/H_2 and CO_2/CO is sufficiently small in the temperature range involved so that no material error will be introduced by a small error in the temperature reading.

In order to avoid confusion, it is customary to make all calculations of free energy values ($\triangle F$) with reference to the standard state, in which the activity is considered unity. For convenience, we shall arbitrarily choose a

[1] *Journal*, Iron and Steel Institute, Vol. 114, p. 295, 1926. I have been able on the basis of their data to evolve a graphical method of obtaining equilibrium constants of very high accuracy, in the temperature range in which the percentage CO_2 is only 0.05. Consult my discussion of a paper by Schwartz on "Some New Aspects of the Iron-Carbon Diagram" being presented at this meeting.

single crystal of pure αFe as the standard state up to 900 degrees Cent. (A_3) and again from 1400 degrees Cent. (A_4) up to the melting point; we shall likewise choose a single crystal of pure γFe as the standard state from 900 to 1400 degrees Cent. Without any sensible error, we shall also consider polycrystalline αFe and γFe to have the same activity as the single crystals. Although Fe and FeO are mutually soluble in each other to a very slight extent, it is sufficient for the present purpose (considering the quality of the data we possess) to assign to solid FeO and to the iron in equilibrium with the FeO, unit activity and to treat them as the standard states. Hence, we are justified in setting up the following equations:

$$FeO + H_2 = \gamma Fe + H_2O;\ \Delta F_1 \qquad (1)$$

$$+ H_2\ \tfrac{1}{2}O_2 = H_2O(g);\ \Delta F_2 \qquad (2)$$

Subtracting equation (1) from equation (2) we obtain

$$\gamma Fe + \tfrac{1}{2}O_2 = FeO;\ \Delta F_3 = \Delta F_2 - \Delta F_1 \qquad (3)$$

In the case of CO/CO_2 gas, we have similarly

$$FeO + CO = \gamma Fe + CO_2;\ \Delta F_4 \qquad (4)$$

$$+ CO\ \tfrac{1}{2}O_2 = CO_2;\ \Delta F_5 \qquad (5)$$

Subtracting equation (4) from equation (5), we obtain again

$$\gamma Fe + \tfrac{1}{2}O_2 = FeO;\ \Delta F_6 = \Delta F_5 - \Delta F_4 \qquad (6)$$

Equations (3) and (6) are standard free energy equations above 900 degrees Cent. up to the melting point of FeO. Below 900 degrees Cent., we have the following free energy equation (of transition of $\alpha \rightleftarrows \gamma$) to consider:

$$\alpha Fe = \gamma Fe;\ \Delta F_7 \qquad (7)$$

Adding

$$\gamma Fe + \tfrac{1}{2}O_2 = FeO;\ \Delta F_3 \qquad (3)$$

we obtain

$$\alpha Fe + \tfrac{1}{2}O_2 = FeO;\ \Delta F_8 = \Delta F_3 + \Delta F_7 \qquad (8)$$

Likewise

$$\Delta F_8 = \Delta F_6 + \Delta F_7 \qquad (9)$$

In the same manner, since most of the previous studies are at temperatures below 900 degrees Cent., instead of the reaction represented by equations (1) and (4) respectively, we really have,

$$FeO + H_2 = \alpha Fe + H_2O;\ \Delta F_{10} \qquad (10)$$

and

$$FeO + CO = \alpha Fe + CO_2;\ \Delta F_{11} \qquad (11)$$

so that when we add equation (7) to equation (10) and (11) respectively, we obtain equations (1) and (4) again. Reversing the process, if we subtract

equation (7) from equations (1) and (4) we obtain equations (10) and (11) respectively. In other words, except for the fact that most of the previous investigations were made by the static methods, which are admittedly susceptible to false equilibria, the results so laboriously and skilfully compiled by Messrs. Murphy, Wood and Jominy would have been quite unnecessary if we had previously obtained free energy equation (7).[2] I hope to publish a paper in the very near future embodying the results of my study on the free energy equation (7).

In studying Fig. 8, I noted the K values at 600, 700 and 800 degrees Cent. of Emmett and Schultz were incorrectly plotted with respect to 1/T and so I have carefully redrawn Fig. 8, assuming that the value of K obtained presumably from Fig. 6 has been correctly calculated. It is quite difficult to approximate the slope of C-D as the last two sets of values are so close together; hence, the derived value of the heat fusion, aside from the fact that it is too high, is at best only a pleasant arithmetical exercise. Moreover, from the constitutional diagram of the System Fe-O_2, FeO (Wüstite) upon melting undergoes a reaction of a peritectic nature, so that the heat of reaction calculated by Messrs. Murphy, Wood and Jominy may be the sum of the heat of fusion of FeO plus the heat of reaction with the melt. Finally in calculating in the heat of reaction according to the slope of C-D (that is, heat of reaction involving liquid FeO), they have assumed the activity of FeO in the melt to be unity, which is very improbable, although it is a close enough approximation to assign unit activity to solid FeO as I have done in setting up the free energy equations.

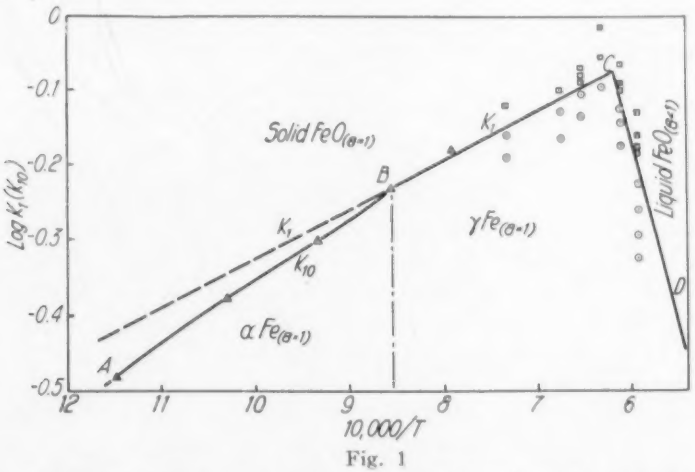

Fig. 1

In drawing B-C, I have taken into consideration the relative positions of the 900 and 1000 degrees Cent. values obtained by Emmett and Schultz. We shall discuss later the fairly large deviation of A-B from the line B-C extrapolated to lower temperatures. The value of $\triangle H$ calculated from the slope

[2]Sometime ago in discussing with a prominent metallurgist the scope of my studies, I mentioned the fact that I was making a study of equation (7). I was quite amazed when he remarked, "What *practical* use do your studies have?" I could only answer at that time, "Of what practical use is the constitutional diagram?" Aside from the importance of equation (7) shown above, I have also shown its importance in my discussion of a paper by Dr. Yensen and Mr. Ziegler being presented at this meeting before the A. I. M. E. (Tech. Pub. No. 427).

of the line B-C is about 3000 cal. Also note in Fig. 1 that the lowest value of C in terms of 1/T is about 6.15, so that the melting point of FeO is located at 1353 degrees Cent. The value of 1358-1360 degrees Cent. obtained in their Fig. 6 is accidental, as the intersection of a curve and a straight line cannot be located with great accuracy. However, considering the probable accuracy of their portable potentiometer, the value of 1353 degrees Cent. should be considered in fair agreement of the theoretical melting point of 1370 degrees Cent.

The equation of the curve B-C in Fig. 1 is $\log K = -644/T + 0.320$. Since we know that $\Delta F = -RT \ln K$, we directly obtained free energy equation (1) as $\Delta F_1 = 2763 - 1.48\ T$. Lewis and Randall[3] give $\Delta F_2 = -57{,}500 + 0.94\ T \ln T + 1.65 \cdot 10^{-3} T^2 - 3.7 \cdot 10^{-7} T^3 + 3.93T$. Subtracting equation (1) from equation (2) we obtain $\Delta F_3 = -60{,}263 + 0.94\ T \ln T + 1.65 \cdot 10^{-3} T^2 - 3.7 \cdot 10^{-7} T^3 + 5.41T$.

Likewise upon redrawing Fig. 9 on a larger scale and drawing B-C in such a manner as to make Schenck's values below 900 degrees Cent. lie below it, I obtain $\Delta F_4 = -5329 + 5.96T$. According to Lewis and Randall, $\Delta F_5 = -67{,}510 + 2.75\ T \ln T - 2.8 \cdot 10^{-3} T^2 + 3.1 \cdot 10^{-7} T^3 + 4.46T$, so that subtracting free energy equation (4) from (5) gives $\Delta F_6 = -62{,}181 + 2.75\ T \ln T - 2.8 \cdot 10^{-3} T^2 + 3.1 \cdot 10^{-7} T^3 - 1.50T$. Fundamentally, these equations really hold only at high temperatures as we have considered the heat of reaction over a short range to be constant, but since it is customary to calculate values of ΔF_{298}, I have also done so, as shown below.

	ΔF_3		ΔF_6	
Authority	25°C.	1000°C.	25°C.	1000°C.
Yap	–56,919	–42,913	–58,208	–43,016
Ralston[4]	–57,472	–42,083		
Eastman[5]		–43,255		

The values of ΔF_3 and ΔF_6 at 1000 degrees Cent. that I have obtained check each other very closely and also check that of Eastman better than the value given by Ralston. My values of ΔF_3 and ΔF_6 at room temperature do not check each other; neither do they check Ralston's value. Since Ralston's value at 1000 degrees Cent. appears to be incorrect, his value at 25 degrees Cent. should likewise be unreliable. Of my two values I am inclined to consider the ΔF_3 value to be more likely the correct one because equation (2) is known to have been more accurately studied than equation (5). Moreover, if Schenck's values are trustworthy, then the values obtained by Messrs. Murphy, Wood and Jominy are in error, because the locus of the Schenck values below 900 degrees Cent. does not lie low enough relative to B-C as would be expected from Fig. 1. I am inclined, however, to give more weight to the results obtained by Messrs. Murphy, Wood and Jominy. Finally, it might be pointed out that the values of ΔF_3 at 25 degrees Cent. is practically without meaning on account of

[3]Thermodynamics and the Free Energy of Chemical Substances. New York, 1923. McGraw-Hill Book Co.

[4]Bureau of Mines Bulletin No. 296, 1929, p. 111-2.

[5]*Journal*, American Chemical Society, Vol. 44, 1922, p. 975.

the long extrapolation involved and of the non-existence of the γ form at that temperature. Of course, once we obtain the free energy equation for the transition of iron: $\alpha \rightleftarrows \gamma$ the extrapolated value may then be converted to ΔF_6.

I hope that in contributing this hastily-written discussion, I have brought up some points of interest not only to Messrs. Murphy, Wood and Jominy, but also to others engaged in similar and related studies. For example, free energy equations (3) and (6) should enable us to predict the degree of carburization and decarburization of steel by carbon oxides in the presence of O_2 or FeO. The time has come, if I may be pardoned for reiterating, when it is imperative for a metallurgist engaged either in practical work or in theoretical research to study thermodynamics. The increasing number of papers of this kind constitutes ample evidence that the metallurgical industry is cognizant of the usefulness of thermodynamic studies, that have been so largely neglected in the past.

Written Discussion: By John Chipman, department of engineering research, University of Michigan, Ann Arbor, Mich.

The authors are to be particularly commended for their determinations of the equilibrium conditions in the scaling of pure iron in gaseous mixtures. To the physical chemist interested in the thermodynamics of high temperature reactions, these data present a new and independent confirmation of the directly observed values for the equilibrium constant in the "water-gas reaction." To the metallurgist they provide the fundamental basis for the control of scaling at high temperatures, while to those interested in the physical chemistry of steel-making, they furnish the first adequate basis for the extrapolation of the free energy of ferrous oxide to steel-making temperatures.

The heat of fusion of ferrous oxide, which appears as a by-product of this investigation, is a constant of fundamental importance in the study of the chemical reactions of this substance in liquid slags. At first glance, the uncertainty of $\pm$ 5000 calories in the value of 28,000 calories reported for this constant might seem unduly large. It should be recalled, however, that this is the first experimental determination of this constant which is even approximately valid. Previous estimates used by investigators of steel-making reactions have ranged from 3600 to 55,000 calories.

Written Discussion: By O. W. McMullan, metallurgical department Timken-Detroit Axle Co., Detroit.

The writer would like to ask if any checks were made on the samples for decarburization. There seems to be a difference of opinion as to whether or not an atmosphere which produces scale is better to prevent decarburization at ordinary hardening temperatures up to forging temperatures. Claims are made that the oxide scale acts as a protective layer at the hardening heats and that the oxidizing atmosphere removes the iron faster than it does the carbon at forging temperatures.

Written Discussion: By H. H. Ashdown, research laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.

The loss of steel due to oxidation in hot working does not in the past appear to have received the attention from the steel manufacturers or furnace builders that might well have been expected. Electrically heated furnaces of large capacity are now in operation for obtaining and maintaining for long

periods temperatures of well over 1000 degrees Cent. for normalizing large masses of steel and the time should not be far distant when they will be available for forging temperatures. In these furnaces a neutral or reducing atmosphere can be maintained and it is along these lines we may hope to achieve a solution to this problem. The loss due to oxidation runs into many thousands of tons per annum and its value to millions of dollars, the loss in the mills due to this cause is about 4 per cent, at the forges, for solid work about 6 per cent and hollow forgings as high as 10 per cent. This surely at this time, must represent the difference between profit and loss and from this angle alone this paper should be appreciated.

Adjustments in existing plant methods for controlling the furnace atmosphere are deserving of attention if a saving of only 25 per cent of this loss can be effected.

This paper contains much material deserving of careful thought and the experiments well worth developing on a practical scale. The temperature of mill ingots often is unnecessarily well above the fusion point of the scale and they lose any advantage that a light fusion of the scale offers in resisting more rapid oxidation, further this fluid oxide is rapidly destructive to the refractories and the fabricated steel is by no means in the best condition.

Where ingots or billets for either rolling or forging require a long soaking period to well soften the center, it would, from the results made known in this paper, appear to be to advantage once a safe temperature has been attained throughout the mass, to raise the furnace temperature for a short period to the fusion point of the scale and form a protective sheath and then lower to a normal soaking heat.

In forge work a dry scale is desired so that the immediate effect of distortion under the forge tools is to crack up the scale which falls away leaving a clean material for working. This is essential as it allows the forgeman to work nearer to the machine size of the job and also prevents the destructive nature of embedded scale on the cutting tools. One point of interest brought out in this paper is the marked reduction in the rate of oxidation of the steels in the higher carbon range. Although the authors' theory for this is not questioned, is this slowing down of oxidation not also accounted for by the rapidly formed and heavily decarburized surface of the high carbon steels? The carbon content of a deep skin on a forging made from a 1.0 per cent carbon steel would rarely contain 0.20 per cent carbon.

The difference in color sometimes to be observed between the inside and outside surfaces of any forging scale and also the scale between low and medium carbon steels may be explained by the authors' hypothesis.

That a marked difference does exist is shown in the accompanying photograph where the ferrite boundaries of the large crystalline structure of the strongly heated billet are outlined in the heavy scale by a much lighter color. This pentagonal outlining corresponds also with the pentagonal honeycomb formation sometimes to be observed in the cavity of large ingots immediately under the sinkhead.

Authors' Closure

The authors desire to express their appreciation to Dr. J. Chipman, H. H. Ashdown, and Yap, Chu-Phay for their remarks in connection with this paper.

Concerning O. W. McMullen's inquiry regarding decarburization at forging temperature, the authors would like to state that no observations on decarburization were made in this study.

Mr. Ashdown has brought out an interesting point in regard to the economic loss entailed by scaling. The advisability of raising the temperature of the soaking furnace above the melting point of the oxide for a short period of time might be open to some question since the scaling becomes very rapid with temperatures sufficiently high to produce liquid oxides.

In advancing the idea that carbon may retard the scaling reaction by maintaining atmospheres rich in carbon monoxide within the scale, the authors would like to point out that the carbon monoxide may be derived both from the steel which has been scaled and from that which has been decarburized.

It will be noted from Table III that the scale formed on the high-carbon steels is of different composition than that formed on the low-carbon steels. That formed on the low-carbon steels approximates Fe_3O_4 and contains practically no FeO, whereas that formed on the highest carbon steel contains a high percentage of FeO. In view of this difference in composition, it does not seem reasonable to explain the lower scaling rate of the highest carbon steel as re-

sulting from the resistance to oxidation of the decarburized low-carbon surface.

The authors wish to thank Mr. Yap, Chu-Phay for calling attention to the incorrect plot of Emmett and Schultz' data but wish to point out the fact that the curve representing their data is correct, since only the actual points were shifted in tracing. These data are correctly plotted in the *Journal of Industrial and Engineering Chemistry*, Volume 23, page 384, 1931. In reply to his question concerning the use of a portable pontentiometer, the authors wish to point out that the accuracy of the portable instrument is well within the accuracy of the thermocouples of ± 5 degrees Cent. in this range. The portable potentiometer was selected for this work partly for convenience and was furthermore checked against a Type K potentiometer.

The authors have no knowledge of previous data which would lead to a more accurate value of the heat of fusion of FeO and it seems that the statement that the heat of fusion as determined in this study is too high is unjustifiable. The possible existence of a peritectic reaction between oxide melts and iron is, of course, recognized but until the existence of that reaction has been demonstrated more conclusively the authors feel justified in making the simplest assumption, namely that FeO possesses a true melting point. Consequently it is felt that the assumption of unit activity for liquid FeO making possible the calculation of the heat of fusion in the absence of other data is justifiable; indeed it seems quite as logical as Mr. Yap's assumption of unit activity for iron in the presence of oxygen which latter we know will dissolve in iron and alter slightly the activity value.

Finally, the authors do not believe that the entire deviation cited by Mr. Yap in his Fig. 1 is due to the reaction $\alpha Fe = \gamma Fe$. The curvature of the line representing equilibria between $Fe:FeO:H_2:H_2O$ arises almost entirely from the changes in the quantity ΔC_p of the reaction. Furthermore, any attempt to explain such deviations by the reaction of $\alpha Fe = \gamma Fe$ omits consideration of the complementary system $Fe:FeO:CO:CO_2$. The determinations of Emmett and Schultz and of Schenck have furnished an excellent check on the direct determination of the water gas equilibria. It seems more than likely that whatever influence the reaction $\alpha Fe = \gamma Fe$ might have upon the equilibria might be entirely masked by the other factors and could consequently lead to an erroneous conclusion regarding the magnitude and sign of that influence.

CEMENTED TANTALUM CARBIDE TOOLS

By Floyd C. Kelley

Abstract

This paper compares the physical and chemical properties of tungsten and tantalum and their respective carbides. The methods of preparation of tantalum carbide and cemented tantalum carbide are described and the physical properties obtained by using various binders are discussed. Comparative tool tests of cemented tungsten carbide and cemented tantalum carbide are given.

THE use of cemented tungsten carbide as a tool material in our larger industries is quite general today. The early work in this field was done by Messrs. Karl Schroeter and Henrich Baumhauer of the Osram Lamp Co., Berlin. Considerable work has also been done during recent years at the research laboratory of the General Electric Company on this most interesting development of cemented metal carbides. The research on cemented tantalum carbide by the Geneneral Electric Company is a development of the work by that company on cemented tungsten carbide. This research has produced some specific results.

Tantalum is found in the fifth group of the periodic table of elements associated with vanadium and columbium. The hardness of the carbides of this group, VC, CbC and TaC is given in the literature as 9+ on Mohs scale. They crystallize with the face-centered cubic lattice. Tantalum has a density of 16.67 while columbium, which is usually found associated with it in the ore and can be separated from it only with difficulty, has a density of about 8.33. The densities of their respective carbides are about 14 and 8.2.

The percentages of carbon in TaC and CbC are 6.2 and 11.4 respectively. The carbides of these elements melt at 3800 degrees Cent. (6870 degrees Fahr.) +. The addition of carbon to tantalum raises its melting point from 2850 to 3800 degrees Cent. + (5160-6870 degrees Fahr.) while the addition of carbon to tungsten lowers

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its melting point from about 3370 to 2900 degrees Cent. (6100-5250 degrees Fahr.) in the case of WC.

Tantalum is very active toward hydrogen, nitrogen, and oxygen at low temperatures, while tungsten is not affected by either hydrogen or nitrogen and does not react so readily with oxygen in the wrought condition as tantalum. Tantalum oxide cannot be easily reduced in hydrogen, while this is the regular process used in obtaining tungsten metal. Bar stock of tantalum can be cold-rolled into thin sheets, but tungsten must be worked while quite hot. Tantalum properly annealed has about the same hardness as annealed copper, while annealed tungsten has a Brinell hardness of about 225. These elements are closely related in the periodic table having nearly the same atomic weights; the atomic weight of tantalum being 181.5 and that of tungsten 184. Their respective densities are 16.67 and 19.3. Despite these differences, the carbide of tantalum (TaC) has, however, been successfully made from both the metal and its oxide in substantially the same way as tungsten carbide used in the manufacture of cemented tungsten carbide.

Preparation of Tantalum Carbide

If the carbide is made from the metal, it has been the practice to use material of a particle size not larger than one hundred mesh. This is mixed with a sufficient amount of carbon to produce TaC, when fired in a hydrogen furnace at 1500 to 1600 degrees Cent. (2730 to 2910 degrees Fahr.) for a period of five to eight hours. The time of firing depends not only on the size of the charge, but also on the particle size. The color of the sintered mass when broken tells its own story. The charge seems to carburize most rapidly at the outside, and gradually progresses toward the center. It has a typical golden lustre at the outside with a gradual shading off into the brown or brownish black at the center when incompletely carburized. The charge when completely carburized exhibits a perfectly uniform crystalline lustre of a golden character.

Hydrogen is undoubtedly responsible for the progressive carburization of the charge from the outside toward the center. As the gas diffuses through the mass of powdered material it picks up carbon, forming hydrocarbons which react much more rapidly with the metal than the carbon in the solid state. This accounts in part for the difference in time required to carburize charges of different size.

When tantalum oxide (Ta_2O_5) is used, enough carbon is mixed with it to reduce the oxide and carburize the resulting metal to TaC. Here again, difficulty is sometimes experienced in securing complete carburization with a heating time of five to eight hours, and especially when large charges are used. In practice the aim is to produce a material which does not vary more than one-tenth of one per cent of the theoretical amount required to form TaC. Good tools may be made, however, with carbides where the carbon varies considerably from this amount.

When oxides from different sources are used, one runs into difficulty due to the presence of columbium which is not easily removed. Columbium is of lower atomic weight than tantalum but combines with the same amount of carbon. If the columbium content of the oxide is not accurately known and the carbon added is based on the assumption that the oxide is Ta_2O_5, the resulting material will not be completely carburized.

We have been fortunate in having the cooperation of Dr. G. R. Fonda of our laboratory who has given us comparatively quick and accurate X-ray spectrographic analyses[1] of our tantalum oxide for columbium by the use of a cathode ray tube, and whenever there was any question about the complete carburization of the materials, due to the presence of columbium, he has been of great assistance. When considerable amounts of columbium are present, the color of the carbide and its density serve as checks on the purity of the material.

Cemented Tantalum Carbide

Various compositions have been used as binder materials. The metals used for these binders have been of the greatest purity obtainable. Many have been made by the hydrogen reduction of the oxides.

The procedure for making up the material out of which bars are pressed has been as follows:

The tantalum carbide is milled after firing to break up the large crystals formed during the carburizing operation until it passes through a 325-mesh screen. The metals for the binders, which have been put through a 325-mesh screen, are mixed in the right proportion by ball milling, or some other suitable method. Then the proper proportions of carbide and binder are mixed together and

[1]Gordon R. Fonda and George G. Collins, *Journal*, American Chemical Society, Vol. 53, 1931, p. 113.

milled for about four or five hours and pressed into bars of the desired shape and size.

In all of the early research work, tantalum metal of the greatest purity obtainable was used to insure uniform and reliable results.

In the early work 13 per cent of binder was generally used to secure as much strength as possible without too great a sacrifice in hardness. An early tool containing cobalt as a binder had a hardness of about 83 Rockwell A and a modulus of rupture of around 100,000 pounds per square inch. The temperature of firing did not seem to change its hardness more than about two points. The tool was easy to grind but had a tendency to chip on the wheels used for grinding cemented tungsten carbide. When tested on cast iron, cold-rolled steel and shafting steel it cut them nicely, but the edge of the tool had a tendency to chip. Here it was noticed that the material had some remarkable qualities for even after the tool was dulled by chipping it showed wonderful resistance to wear.

When iron was used as a binder we obtained a hardness of about 84 Rockwell A and a modulus of rupture of about 120,000 pounds per square inch. This tool ground very easily and took a keen cutting edge. When tested on cast iron and steel it gave a nice finish and cut the steel instead of pushing it off.

An early tool containing nickel as a binder had a hardness of about 82 Rockwell A and a modulus of rupture of 170,000 pounds per square inch. It took a very keen edge and was able to cut nickel steel for twenty minutes at a speed of seventy feet per minute with a feed of 0.025 inch and a depth of cut varying from ⅛ to ¼ inch without showing wear. When deeper cuts and heavier feeds were used it had a tendency to mushroom and wear.

The next step was an attempt to increase both the strength and hardness through the use of modified binders. Sample test bars made up with each binder to secure the modulus of rupture and hardness of the various compositions. The firing temperature was varied for each binder to insure maximum sintering, strength, and hardness. Duplicate tools were made from those compositions which showed the best combination of strength and hardness. The tool tips were mounted on ¾ x 1½ inch nickel steel shanks by copper brazing in a hydrogen furnace. These tools were ground the same as standard cemented tungsten carbide tools for comparison.

In order to measure the quality of cemented tungsten carbide

Table I
Tool Cutting Tests

Tool No.	Depth Cut Inches	Feed Inches	Speed	Duration	Remarks
1	3/8	0.055	90 ft.	8 min. 47 sec.	Edge in excellent condition and still very sharp.
1	3/8	0.055	100 ft.	10 min.	Edge still in excellent condition.
Duplicate					
1	1/32	1/64	250 ft.	10 min.	Edge not worn. Finish on log very good.
1	1/32	1/64	180 ft.	20 min.	Edge not worn. Very satisfactory finish on log.
2	3/8	0.050	70 ft.	10 min.	Edge not worn.
3	3/8	0.050	70 ft.	10 min.	Edge slightly worn.
4	3/8	0.050	70 ft.	10 min.	Edge showed no wear, but chipped and cracked back of cutting edge.
Duplicate					
4	1/16	1/64	140 ft.	3 min.	Edge and cut excellent.
4	1/16	1/64	180 ft.	7 min.	Edge and cut excellent.
4	1/8	1/64	200 ft.	10 min.	Edge and cut excellent.
4	1/8	1/64	250 ft.	10 min.	Edge and cut excellent.
4	1/8	1/64	300 ft.	10 min.	Edge showed slight wear. Finish on log better at 180 ft.
5	3/8	0.050	70 ft.	10 min.	Edge good but slightly mushroomed.
6	3/8	0.050	70 ft.	10 min.	Edge in as good condition as No. 4, but not cracked.
7	3/8	0.050	70 ft.	10 min.	Edge in good condition, but end slightly mushroomed.

tools, a standard test has been adopted which consists of a 10-minute run on a 3½ per cent nickel steel log having a hardness of about 195 Brinell at a speed of 70 feet per minute with a 3/8-inch depth of cut and a feed of 0.055 inch. Some of the results of tests on the above tools under these conditions are given in Table I.

The modulus of rupture and hardness of the early tools were considerably lower than the modulus of rupture and hardness of cemented tungsten carbide tools, and showed conclusively that the properties of a good tool do not depend entirely upon its strength and hardness. These tools, in general, could be ground more easily than cemented tungsten carbide. They could be ground on ordinary grinding wheels and much keener cutting edges obtained.

When cutting nickel steel they maintained their sharp cutting edges under severe working conditions for relatively long periods of time. There were no signs of wear just back of the cutting edge where the chip curls up on the top of the tool as is sometimes the case with the cemented tungsten carbide tools. The finish on the log was smooth, but not burnished, showing that the edge of the tool

was cutting and not pushing or tearing the metal off. The chip came off cool compared with one removed by a cemented tungsten carbide tool. It required a few seconds to color up to the same blue exhibited by a chip as it left the cemented tungsten carbide tool. The difference in cutting efficiency was evidenced by the fact that, when the limit of speed which could be obtained in removing a certain size of chip was reached with the cemented tungsten carbide tool, it was possible to remove a chip of the same size at a much higher speed with the cemented tantalum carbide tool.

Tool No. 1 showed almost no bluing of the shank just underneath the copper brazed joint and, after removing a chip of 0.050 x ⅜ inch for ten minutes, could be held in the hand at the cutting end. A cemented tungsten carbide tool removing the same chip would be discolored about one-half way down the tool under the joint and would be about as hot at the cooler end as the tantalum carbide tool was at the cutting end.

Tool No. 6, showed a discoloration beneath the joint, but equal to about one-half the distance discolored on the cemented tungsten carbide tool. Later it was observed that the amount of discoloration obtained varied with the binders also.

Cemented tantalum carbide has a lower coefficient of friction than cemented tungsten carbide, which shows up in the amount of power required to remove a chip of a definite size, and also in the amount of heat generated in the tool. The material after firing has a feeling much like that of soap stone. This low coefficient of friction resulting in lower temperature of operation of the tool undoubtedly accounts for the difference in the wear just back of the cutting edge where the chip curls up. It also accounts for the preservation of the sharp cutting edge, for there is seldom any seizure between the material being turned and the tool tip, as is sometimes the case in cemented tungsten carbide when used to cut steel. Under severe cutting conditions it often approaches seizure although the steel which sticks to the cutting edge can be removed without injury to the tool.

Comparative tests of cemented tungsten carbide and cemented tantalum carbide on 3½ per cent nickel steel with 0.35—0.40 per cent carbon and a Brinell hardness of 219, using a $\frac{5}{16}$-inch cut, 0.025-inch feed and a speed of 180 feet per minute showed that the average life of the cemented tungsten carbide tools containing 13 per cent cobalt as a binder was 15.4 minutes and of those containing 6 per cent cobalt was 26.2 minutes.

Table II
Physical Characteristics of Cemented Tantalum Carbide

Sample No.	1	2
Density	13.6	12.6
Rockwell A hardness	84	89
Modulus of Rupture in lbs. per sq. in.	192,000	120,000
Conductivity in megamhos	0.035	0.016
Temperature Coefficient in ohms per ohm per degree Cent.		
Degrees Cent.		
25—102	+0.00119	+0.00238
25—198	+0.00153	+0.00249
25—303	+0.00162	+0.00261
25—399	+0.00178	+0.00284
25—500	+0.00171	+0.00247
Heat conductivity compared with Norway Iron		
38—90 degrees Cent.	0.68 of Norway iron at 20—35 degrees Cent.	
30—50 degrees Cent.		0.40 of Norway iron at 14—70 degrees Cent.
Elastic Modulus	58,000,000	

The cemented tantalum carbide tools tested under the same conditions ran up to forty minutes without any sign of break-down and looked as if they were capable of turning up the entire log. It was necessary in most cases in order to save time and material, to run the tools for twenty-five minutes, a period about equal to that of the longest average life obtained on cemented tungsten carbide tools, and then draw conclusions as to their performance.

It must be remembered that these comparisons have been made on nickel steel and no claim has been made that cemented tantalum carbide is superior to cemented tungsten carbide as a tool for general use. Many cemented tantalum carbide tools have been tested on steel under shop conditions at relatively high speeds and the most striking observations are the fine finish, uniform size of the material turned over long sections, the ease with which the material is removed, and the long life of the tool due to the reasons stated.

Physical Characteristics of Cemented Tantalum Carbide

The physical characteristics of cemented tantalum carbide can be varied greatly by changing the composition of the binder, as is shown by data in Table II. Sample No. 1 contains 87 per cent TaC with 13 per cent of the binder (25 WC, 75 Co) and sample No. 2

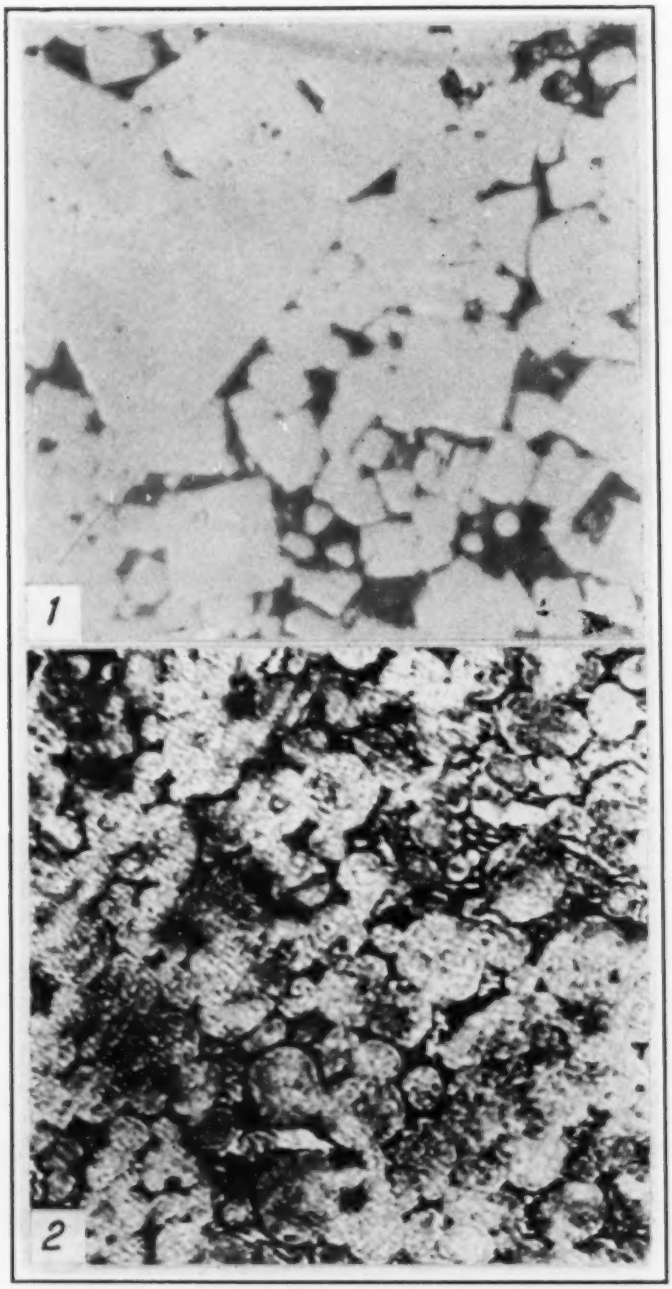

Fig. 1—Cemented 87 Per Cent Tantalum Carbide with 13 Per Cent of the Binder (25 WC, 75 Co). × 1500.
Fig. 2—Cemented 87 Per Cent Tantalum Carbide with 13 Per Cent of the Binder (37 Mo, 63 Fe). × 1500.

contains 87 per cent TaC with 13 per cent of the binder (37 Mo, 63 Fe). The sintering temperature of both is 1400 degrees Cent. (2550 degrees Fahr.) for one and one half hours.

Representative photomicrographs of Samples 1 and 2 are shown in Figs. 1 and 2 respectively. Fig. 1 shows a structure very similar to cemented tungsten carbide. Grain growth occurs during the firing

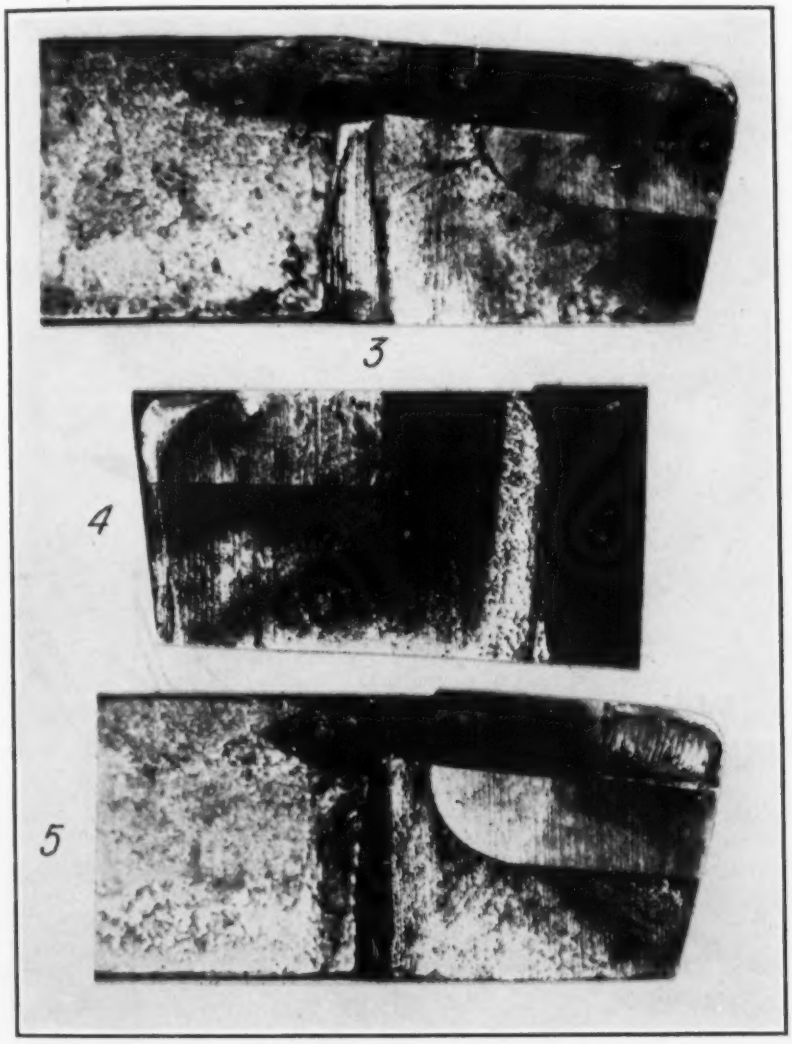

Fig. 3—Cemented Tungsten Carbide with 13 Per Cent of Cobalt as the Binder. × 2.5.
Fig. 4—Cemented Tungsten Carbide with 13 Per cent of Cobalt as the Binder. × 2.5.
Fig. 5—Cemented Tungsten Carbide with 6 Per Cent of Cobalt as the Binder. × 2.5.

operation and many of the grains formed are well defined, being nearly square or rectangular in cross-section. Fig. 2 shows very little grain growth and the carbide particles have taken on a spherical form which may account for the lower modulus of rupture of this

material. The shapes of these particles show that the cementing material has attacked each particle leaving it in a spherical form.

The wear resisting quality of cemented tantalum carbide compared with cemented tungsten carbide containing 13 per cent of cobalt

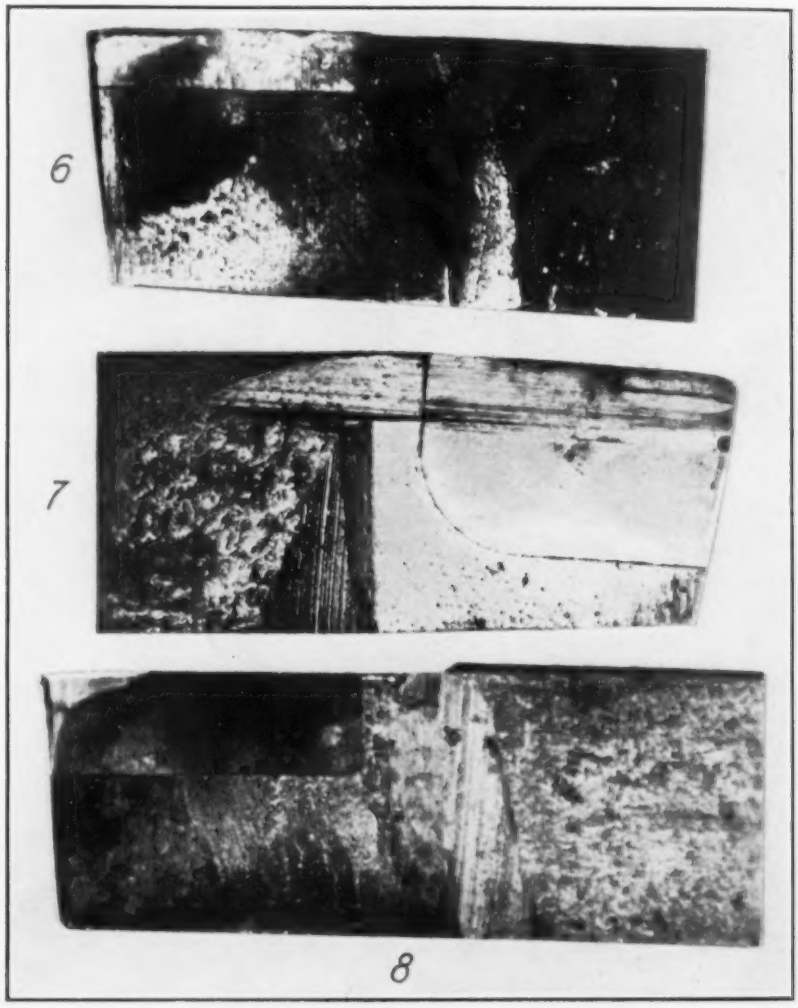

Fig. 6—Cemented Tungsten Carbide with 6 Per Cent of Cobalt as the Binder. × 2.5.
Fig. 7—Cemented Tantalum Carbide with 13 Per Cent of (25 Tungsten Carbide, 75 Cobalt) Binder. × 2.5.
Fig. 8—Cemented Tantalum Carbide with 13 Per Cent of (25 Tungsten Carbide, 75 Cobalt) Binder. × 2.5.

and 6 per cent of cobalt is illustrated in Figs. 3 to 8. They show the results of tests on duplicate tools made on 3.5 per cent nickel steel with Rockwell hardness of 195 Brinell at a speed of 200 feet per

minute with a $\frac{3}{16}$ inch depth of cut and a feed of 0.020 inch. The duration of these tests was ten minutes in each case.

Figs. 3 and 4 are photographs of two different cemented tungsten carbide tools containing 13 per cent of cobalt binder. Fig. 3 shows the slightly mushroomed nose which is worn and the crater developed on the top of tip due to the friction and seizure of the chip where it curled up on the tool tip. Fig. 4 shows the wear on the front cutting edges and noses of the tool.

Figs. 5 and 6 are photographs of two cemented tungsten carbide tools containing 6 per cent of cobalt. The craters on the top of these tools are much more distinct due to the fact that these tools did not mushroom, and there is much less wear on the front cutting edges and the tips of these tools.

Figs. 7 and 8 are photographs of tools made from material whose microstructure is revealed in Fig. 1. Fig. 7 shows a polished area on the top of the tip where the chip curled up but there is no crater. Fig. 8 shows the keen cutting edge and the sharp outline of the unworn cemented tantalum carbide tools.

The final composition for such a tool material will be determined ultimately by long use and experience under manufacturing conditions, and by new developments and progress in the art of fabricating the cemented tantalum carbide.

DISCUSSION

Written Discussion: By Clarence W. Balke of the Research Laboratories of the Fansteel Products Co., Inc., Chicago.

We have read the paper of Floyd C. Kelley on cemented tantalum carbide with much interest since a great amount of research work on tantalum carbide tools has been done in the laboratory of the Fansteel Products Co. and this has been an expansion of the tantalum industry pioneered in this country by that company. During our investigation we prepared several hundred distinct lots of material containing tantalum carbide, and we studied these individual lots as to hardness, strength, and other physical properties, as well as the performance of the material when used as a cutting tool. Much of our early work is confirmed by the results reported by the author in reference to hardness, strength, and performance of tantalum carbide tools. We have devoted a large amount of time to perfecting a technique for the manufacture and handling of tantalum and its fabrication into cutting tool material. While it is hardly within the scope of this discussion to attempt to enter into an account of the vast array of detail which has been involved in this investigation, I feel that the cutting tests reported in the paper do not adequately convey the possibilities of tantalum carbide tools.

While a tool having a Rockwell A hardness as low as 84 will function in a satisfactory manner when turning relatively soft materials, it will fail almost immediately when turning hard materials such as chilled cast steel, or 12 to 14 per cent manganese steel. The following tests have been obtained recently with a tool having a Rockwell A hardness of somewhat more than 90, and a modulus of rupture as high as 214,000 pounds, and notwithstanding this high hardness the tool could be ground to a very keen edge with no tendency of chipping:

This tool turned the entire length of a cast steel roll practically file hard, 8 inches in diameter and 27 inches in length, using ⅛ inches depth of cut, 0.031 feed, and a speed of 34 feet. The tool showed only a slight top wear at the conclusion of the test and was considered in good condition.

This tool turned the entire length of a 12 to 14 per cent manganese steel roll, 43 inches long, with a feed of 0.010 and a speed of 100 feet. The cutting time of this test was about one hour, and during much of this period the tool was cutting through blowholes and sand pockets which are often characteristic of this kind of steel, yet at the end of this time the tool was found to be in good condition, showing but slight wear on the cutting edge.

This tool was used to make the roughing cut on a cast iron test log 8 inches in diameter and 4 feet long and provided with four keyways 1 inch wide the entire length of the log. The feed was 0.017, the depth of cut 1-16 to ¼ inch and the speed 200 feet per minute. After taking a cut the entire length of the log, the tool was still in good cutting condition and showed only slight deterioration of the cutting edge.

While the work so far done on hard carbide alloys probably represents but a beginning of the great amount of research which will be required to make tools of this type perform at their greatest capacity, there is no question that this work indicates that tantalum carbide will retain a permanent place in this art.

Oral Discussion

Dr. S. L. Hoyt:[1] Mr. Kelley has presented an interesting discussion of a recent development in the art of powder metallurgy of cemented products, particularly the cemented carbide products, and I am sure it is typical of what we may expect from that branch of metallurgy in the future. The principal reason for this, I believe, is that this particular field of metallurgy enables one to prepare, synthetically, structures of these hard compounds which it would be extremely difficult to prepare by the usual methods used in the older type of metallurgy. In other words, the structure of the product is under control. The utility of tantalum carbide, I believe, is brought out by Mr. Kelley's paper and has been attested to by Dr. Balke. It is almost peculiarly adapted to the machining of steel, and the reason for this is the fact that the hot steel chip in passing over the cutting edge does not adhere to the cutting edge of the tool. That is reflected in the soapy feeling of the tantalum carbide tool that Mr. Kelley mentioned. That circumstance must give tantalum carbide a real advantage in machining steel. In machining other metals, such as cast iron, or

[1]Research laboratories, A. O. Smith Corporation, Milwaukee.

in general the abrasives, possibly we should expect somewhat different results, and personally I would expect different results largely from the Rockwell hardness number that Mr. Kelley reports. Dr. Balke did not discuss this effect on his tool, but I expect with a Rockwell A hardness of 90 or above that cemented tantalum carbide would show a better performance on cast iron for instance than a tool which had a Rockwell hardness of only 84, the principal item here being simply of abrasion or wear. I say that I would expect that to happen—I think we know altogether too little about this field to be able to predict such a thing as this with any degree of confidence.

Mr. Kelley has mentioned the preparation of tantalum carbide, and, inasmuch as the author states it is very active towards hydrogen, nitrogen, and oxygen at low temperatures, I believe he has touched upon an extremely interesting phase of the use of tantalum carbide. I would gather from the paper that tantalum carbide would be made similarly to tungsten carbide, and that, of course, would be true if one starts from tantalum metal powder, but if one were to start from tantalum oxide, then I would expect the fact that tantalum metal is active towards hydrogen, and furthermore that tantalum oxide cannot be easily reduced in hydrogen, to become an important factor in the manufacture of the carbide, and possibly Mr. Kelley would expand a little on his own discussion of the manufacture of tantalum carbide by pointing out how it is that the tantalum oxide is to be used in the manufacture of the carbide due to its action toward hydrogen and its nonreducibility in hydrogen.

Mr. Kelley suggests a mechanism for the carburization of tantalum to produce tantalum carbide which, it seems to me, is open to some question, namely that it is due to the diffusion of hydrogen through the charge from the outside and the gaseous carburization of tantalum by the action of hydrogen on the carbon present and the subsequent carburizing. I would be inclined to expect the low thermal conductivity of a power material as being mainly responsible for the coring effect which is noticed when the time of carburization is less than the 5 to 8 hours which Mr. Kelley mentions.

The question of physical properties of these products is extremely interesting. With high speed steel, the properties are more or less fixed, that is, we have a certain hardness and a certain thermal conductivity, etc., and there is no way of varying these materially. Cemented tungsten carbide gives a new set of properties; cemented tantalum carbide gives again a new set of properties; and I believe that in the future those who are interested in tool performance should get an extremely large amount of interesting information covering the factors which affect tool performance, if they will study high speed steel, cemented tungsten carbide, and cemented tantalum carbide and other tool materials with particular reference to the physical properties, and such a study is certainly bound to assist in the work which is being done to develop new compositions and to apply old compositions to all purposes.

In closing I would like to congratulate Mr. Kelley on the work that he has done here. I happened to know something about it while it was going on, and I believe he has shown a great amount of resourcefulness, not only in handling this more or less refractory product, tantalum carbide, but in developing certain materials which improve the physical properties of this material.

Author's Closure

It is gratifying to know that the results revealed in this paper agree so well with those obtained by members of the Fansteel Products Co. research laboratories. No attempt has been made to reveal the extensiveness of the investigation of this particular field by the General Electric research laboratories, for it has been immediately associated with the development of cemented tungsten carbide and the art of cementing hard carbides in general. It must also be remembered that this paper deals only with tantalum carbide plus a binder, and no attempt has been made to underestimate or predict future possibilities for tools of other compositions.

Experience to date indicates in general that where a tool must withstand both shock and extreme abrasion such as are encountered in the rough surface of cast iron that cemented tungsten carbide is superior to cemented tantalum carbide. It is well known to us that cemented tantalum carbide may be modified and a product obtained which will give the performance on cast steel, manganese steel and cast iron mentioned in Dr. Balke's discussion.

It might be pointed out that cemented tungsten carbide tools cut the tough, nonmagnetic, manganese steel without showing much wear on the cutting edge or developing a crater on the top of the tool such as has been described previously. This applies to the tools with the 13 per cent cobalt binders operating under conditions almost identical to those described by Dr. Balke. The feed was 0.013 of an inch with a ¼ inch cut at 100 feet per minute. The smooth work-hardened chip which comes from the log does not seem to seize and drag on the cemented tungsten carbide tip as does a chip from shafting steel or nickel steel.

It is agreed that cemented tantalum carbide will retain a permanent place in the field of metal cutting, and at present the indications are that this place will be in cutting steel.

I wish to thank Dr. Hoyt for his kind comments and the interest he has shown by discussing this paper.

In regard to Dr. Hoyt's remarks concerning the production of tantalum carbide from the oxide, I should say it is well known that metal oxides in general can be reduced by carbon, and the excess carbon above that required for reduction, in this case, serves to carburize the resulting metal, forming its carbide. The latter part of this reaction is the same as the one obtained when the metal plus carbon is used to form the carbide.

Dr. Hoyt's idea of the low heat conductivity of tantalum accounting for the nonuniform carburization of the charge, I do not believe is allowable because of the long firing time (about eight hours) required to secure complete carburization. It is also noticed that this nonuniformity occurs even in small charges. The reaction reminds one of the reduction of iron oxide in hydrogen where the reaction occurs first at the outside and gradually proceeds toward the center. The heat conductivity may be a contributing factor, but certainly is not the major cause of nonuniform carburization. There may be some other factors which influence the reaction, such as sintering, the packing of the particles, etc., but I believe hydrogen is the controlling one.

THE RESISTANCE TO WEAR OF CARBON STEELS

By Samuel J. Rosenberg

Abstract

A study was made of the effect of heat treatment and carbon content upon the wear-resistance of carbon steels as determined by the Amsler machine (combined rolling and sliding friction under heavy pressures). Annealed steels gave poor wear-resisting qualities unaffected by carbon content. Normalized steels showed less wear-resistance in the low-carbon range than the annealed steels, but in the high-carbon range approached the relatively high wear-resistance of the hardened steels. Hardened steels showed a very rapid increase in wear-resistance with increased carbon content, this increase becoming relatively small after about 0.6 per cent carbon. Tempering a hardened steel resulted in a gradual lowering of the wear-resistance. Microstructures of the steels adjacent to worn surfaces showed that this particular type of wear (combined rolling and sliding friction under heavy pressures) was generally accompanied by severe distortion of the structure. A martensitic-troostitic matrix was the most resistant to wear. Steels containing lamellar pearlite showed excellent wear-resistance, while steels containing granular pearlite had poor resistance to wear. The presence of free ferrite, or of free cementite as spheroids, is detrimental to the wear-resistance.

THE resistance of carbon steels to abrasion by sand as determined by the Brinell machine has been reported in a previous paper.[1] As a continuation of this work, this paper reports a study of the resistance of carbon steels to metal-to-metal wear against a hardened eutectoid carbon steel under combined sliding and rolling friction.

[1]Samuel J. Rosenberg, "The Resistance of Steel to Abrasion by Sand," Bureau of Standards Journal of Research, Vol. 5 (R. P. 214), Sept. 1930; also Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 1093.

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A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, Samuel J. Rosenberg, is a member of the society. He is associate metallurgist with the U. S. Bureau of Standards, Department of Commerce, Washington, D. C. Manuscript received May 11, 1931.

I. Method of Test

The apparatus used in this investigation for the evaluation of wear-resistance was the Amsler machine. This machine has been described in detail in a previous paper.[2]

The test specimens used were in the form of small cylinders, 2 inches in diameter and 0.4 inch thick. The specimens were all finish-ground to size. The finished surfaces were produced by wet grinding with a medium hard No. 46 wheel.

All steels were tested against an arbitrarily selected "standard" steel. This standard was an 0.81 per cent carbon steel normalized at 810 degrees Cent. (1490 degrees Fahr.), water-quenched from 780 degrees Cent. (1435 degrees Fahr.), and tempered at 260 degrees Cent. (500 degrees Fahr.). The Rockwell "C" scale hardness resulting from this treatment was just under 60. In all tests the "standard" specimen was mounted on the lower shaft of the machine, which was rotated at about 220 revolutions per minute. The test specimen was mounted on the upper shaft, its speed being about 200 revolutions per minute. In addition to the slip resulting from this difference in speed, the cam which is available on the Amsler machine for producing lateral motion of the upper specimen was used.

All tests were made in duplicate and a new "standard" specimen was used for each test specimen. Wear was measured by the losses in weight of both the specimens.

II. Results of the Test

1. Film Formation

The formation of surface films on specimens tested in the Amsler machine is a familiar phenomenon. In the case of the wear of steel against steel, this film appears to be an oxide of iron and to act as an abrasive. Fink[3] has shown that the partial or complete removal of this film causes a decided decrease in the rate of wear. He tested carbon steels in the Amsler machine under atmospheric conditions and found that a considerable amount of wear took place. When the

[2]H. J. French, S. J. Rosenberg, W. LeC. Harbaugh, and H. C. Cross, "Wear and Mechanical Properties of Railroad Bearing Bronzes at Different Temperatures," Bureau of Standards Journal of Research, Vol. 1, (R. P. 13), Sept. 1928.

[3]M. Fink, "Wear Oxidation, a New Component of Wear," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 204.

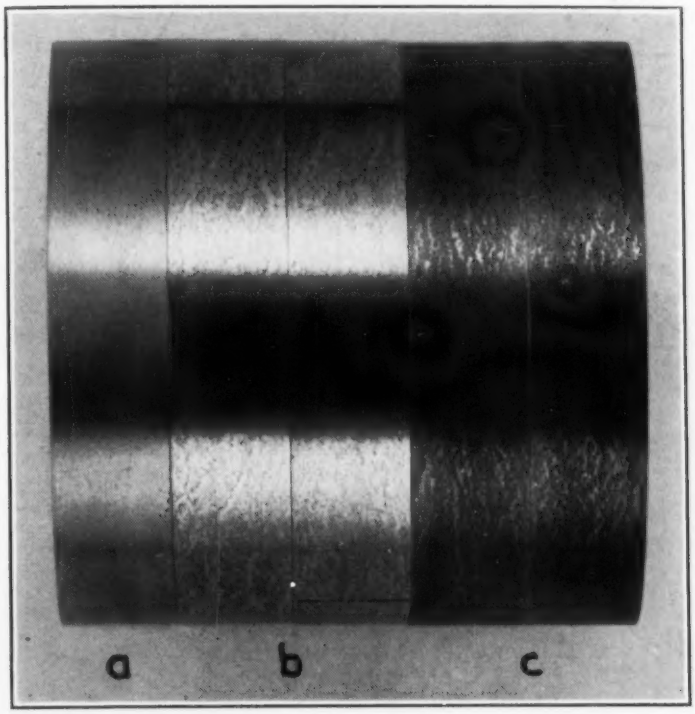

Fig. 1—Appearance of Specimens Before and After Test. All specimens are 0.81 per cent carbon, water-quenched and tempered at 260 degrees Cent. (500 degrees Fahr.). Test load was 60 kilograms.

a. Original ground surface.
b. Appearance of upper specimen (light film).
c. Appearance of lower specimen (heavy film).

same steels were inclosed in a gas-tight cell filled with nitrogen and tested under the same conditions of speed and pressure as before, no wear took place, the test surfaces being smooth and bright at the end of the test. These films are a natural result of the rolling and sliding abrasion of steel against steel under heavy pressures in the presence of air and the absence of lubrication. No attempt was made to remove films during the tests reported in this paper.

When two specimens of the same steel which have also been given the same heat treatment are tested in the Amsler machine, the upper specimen, which travels at the lower angular velocity, loses more weight than the lower specimen. The appearances of the films produced are quite different; the lower specimen has a much heavier film. The films produced on steels of like composition and treatment are shown in Fig. 1. Since it is the lower specimen which forms the heavier film and the upper specimen which suffers the greater loss in

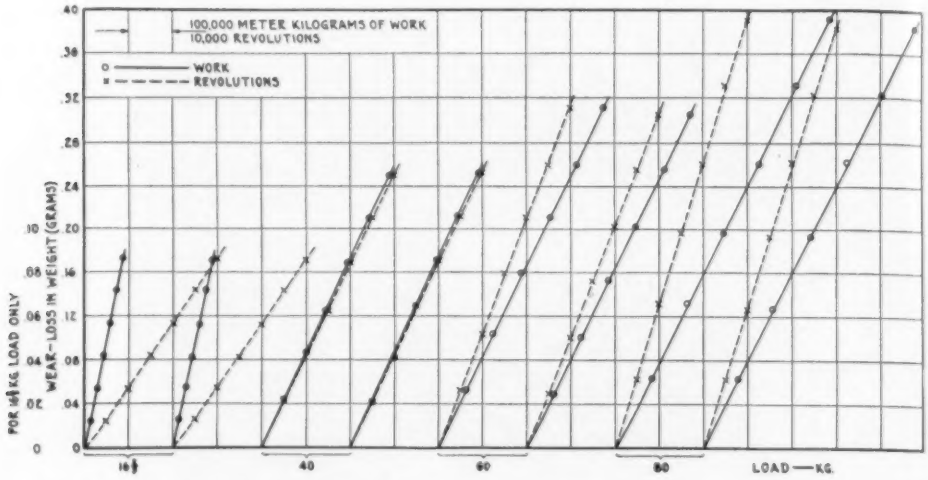

Fig. 2—Typical Wear-revolutions and Wear-work Curves. The specimen tested was a "standard" specimen.

weight, the "standard" specimen was mounted on the lower shaft.

A possible explanation for the difference in losses of weight of two specimens treated alike lies in the fact that the lower specimen forms the heavier film. This film, which acts as an abrasive on the upper specimen, exerts a certain protective influence on the lower one.

2. *Interpretation of Test Data*

The weight loss of the upper (test) specimen was plotted against the revolutions of the lower (standard) specimen to show the relation of wear to slip. This may be conveniently expressed as weight lost per 10,000 revolutions, which was the ordinary duration of a test period. By plotting the weight loss against the work, as calculated from the integrating device on the Amsler machine, the wear per unit of work may be obtained.

Under similar conditions of test, the evaluation of wear by either method generally gives quite similar results. Results more truly indicative of the materials are obtained, however, when the wear is correlated with the frictional work which caused it. For this reason, all comparisons of materials tested are based upon the wear per unit of work. Fig. 2 illustrates wear-revolutions and wear-work curves.

3. *Effect of Pressure Between the Test Specimens*

A series of tests was made with two sets of "standard" specimens tested against each other to determine the effect of increasing

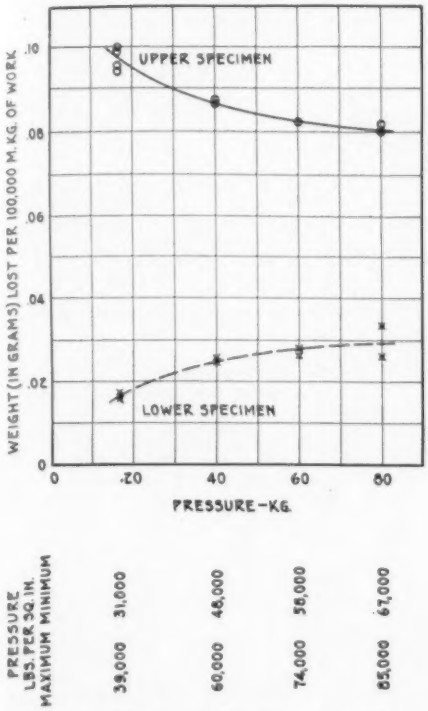

Fig. 3—Effect of Pressure on Wear Per Unit of Work.

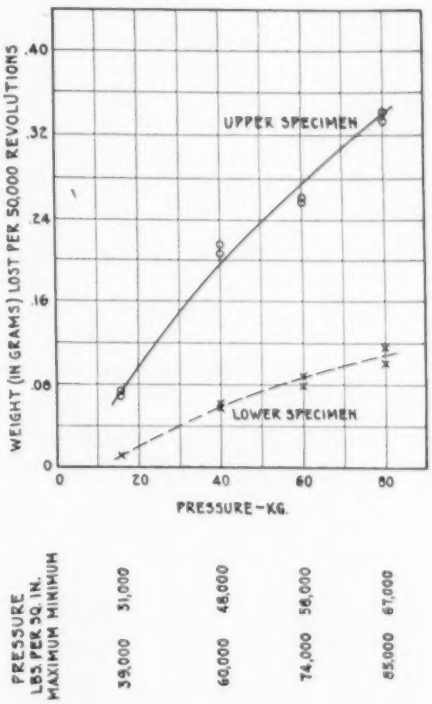

Fig. 4—Effect of Pressure on Wear Per Distance Travelled.

pressure between the specimens. The experimental data of this series of tests are shown in Fig. 2. The comparative results of these tests are shown in Figs. 3 and 4.

The wear per unit of work of the upper specimen decreased as the pressure increased, this decrease becoming less with increasing pressure. The lower specimen, on the other hand, showed an increased amount of wear per unit of work as the pressure increased. This would seem to indicate that, were the pressure sufficiently great, the upper and lower specimens would both lose the same amount of weight. This, however, seems improbable because the curves show evidences of becoming asymptotic. Unfortunately, the frictional torque developed under a total load of 80 kilograms was so great that if a higher pressure had been used, the counterweights would not have been sufficiently heavy to balance the torque developed and no measure of the work could have been obtained. As would be expected, the wear per unit of distance travelled increased with the pressure, both in the upper and lower specimens.

For the tests described in this report, a total load of 60 kilograms was chosen as a standard load under which all tests were made. This

corresponds to a maximum pressure of 74,000 pounds per square inch as calculated from Hertz' formulae.[4]

4. *Materials Tested*

The materials tested were all plain carbon steels, chosen so as to give a range from low to high carbon content. Three series of tests were made, namely, of the steels as normalized, as normalized and annealed, and as normalized, water-quenched, and tempered at 260 degrees Cent. (500 degrees Fahr.). This tempering treatment was necessary in the case of the higher carbon steels in order to prevent any cracking which might otherwise have occurred. In order to keep the treatments uniform, all of the quenched steels were given the same tempering treatment.

Table I
Compositions and Heat Treatments of the Steels Tested

	C	Mn	P	S	Si	Temperature					
	Per	Per	Per	Per	Per	Normalizing		Hardening		Annealing	
Mark	Cent	Cent	Cent	Cent	Cent	°C.	°F.	°C.	°F.	°C.	°F.
M33	0.12	0.44	0.020	0.021	0.25	960	1760	930	1705	910	1670
M35	0.34	0.68	0.024	0.033	0.22	890	1635	860	1580	840	1545
M22	0.58	0.29	0.014	0.018	0.27	825	1515	795	1465	775	1425
EU	0.81	0.23	0.024	0.021	0.28	810	1490	770	1420	755	1390
M48	1.00	0.29	0.018	0.016	0.13	810	1490	770	1420	755	1390
M52	1.26	0.39	0.024	0.018	0.28	925	1695	770	1420	755	1390

Time of holding at normalizing and tempering temperatures, 1 hour.
Time of holding at annealing and hardening temperatures, ½ hour.
All hardening by water quenching, followed immediately by tempering at 260 degrees Cent. (500 degrees Fahr.).

In addition to these tests, a further series of tests was made upon the 0.81 per cent carbon steel to study the effect of tempering temperature between 260 degrees Cent. (500 degrees Fahr.) and 600 degrees Cent. (1100 degrees Fahr.). The chemical compositions and heat treatments of the steels tested are given in Table I.

5. *Effect of Carbon Content on the Resistance to Wear*

The results of the tests on annealed, normalized, and hardened steels, with the Rockwell hardnesses, are summarized in Fig. 5.

The carbon content apparently had little effect upon the wear of annealed steels. Rather surprisingly, the wear of the low-carbon normalized steels was greater than that of the annealed steels of sim-

[4]These formulae and methods of calculation are given in the reference noted in footnote 2.

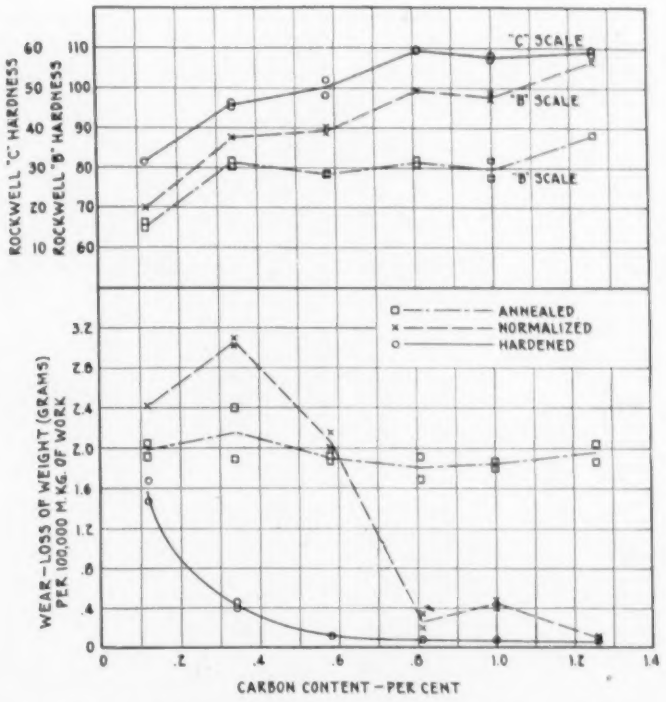

Fig. 5—Effect of Carbon Content on the Wear of Carbon Steels Tested in the Amsler Machine.

ilar carbon content, but with increasing carbon content the wear rate of the normalized steels decreased rapidly, approaching, in the high carbon range, the relatively high wear-resistance of the hardened steels. The wear of the hardened steels decreased rapidly and regularly with increasing carbon content in the lower ranges of carbon. In the higher ranges, however, increased carbon did not materially affect the wear-resistance.

The microstructures of the annealed steels are shown in Fig. 6, the normalized steels in Fig. 7, and the hardened steels in Fig. 8.

6. *Effect of Tempering Temperature on the Resistance to Wear*

The effect of tempering temperature on the resistance to wear of the 0.81 per cent carbon steel was studied. An attempt was made to test this steel as hardened and also as tempered at 150 degrees Cent. (300 degrees Fahr.), but trouble was experienced due to cracking of the specimen. The results of the tests, together with the hardness determinations, are summarized graphically in Fig. 9. These curves show that increase in tempering temperature progressively

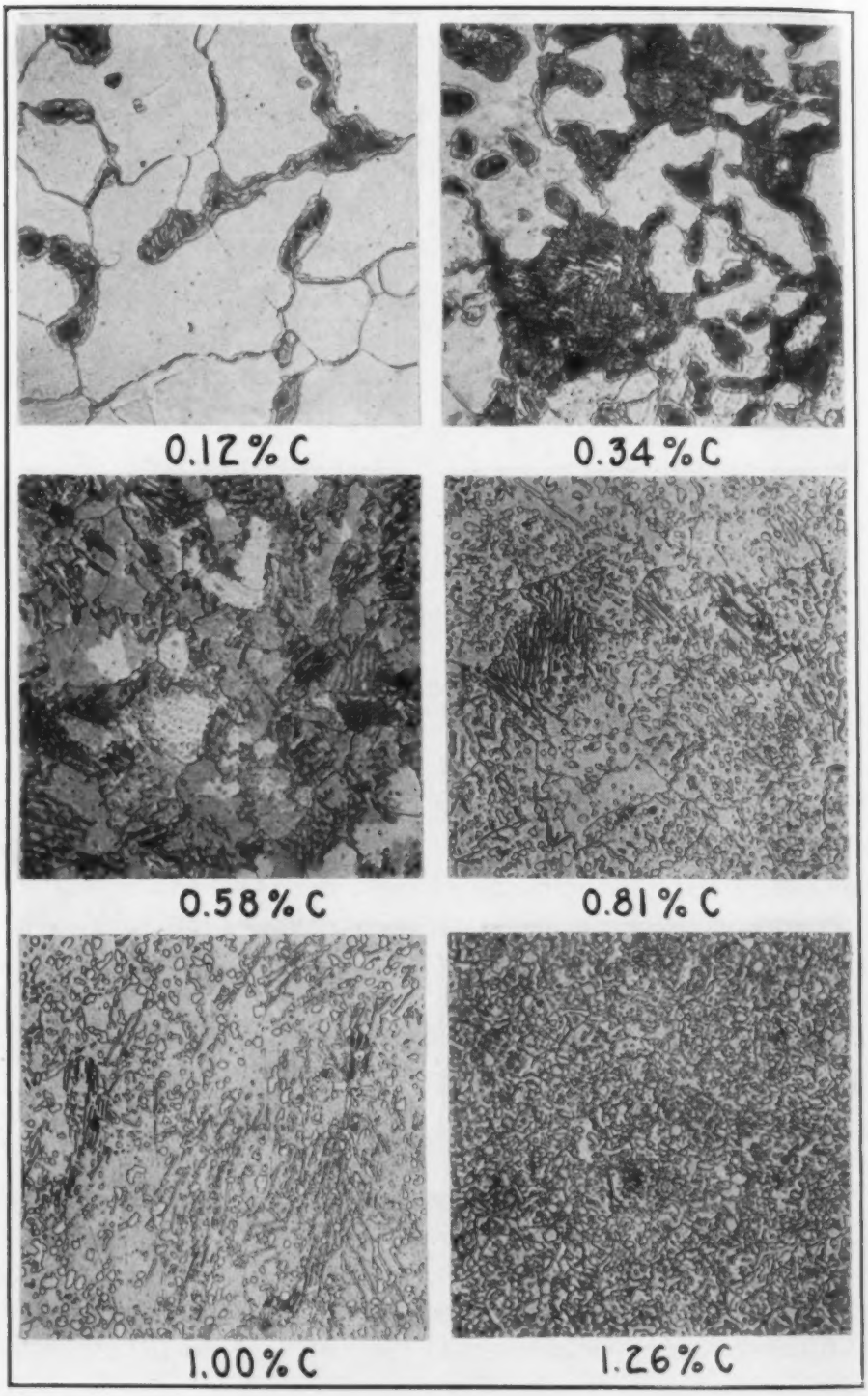

Fig. 6—Microstructures of the Annealed Steels, × 500. Etched with 2 per cent nitric acid in alcohol.

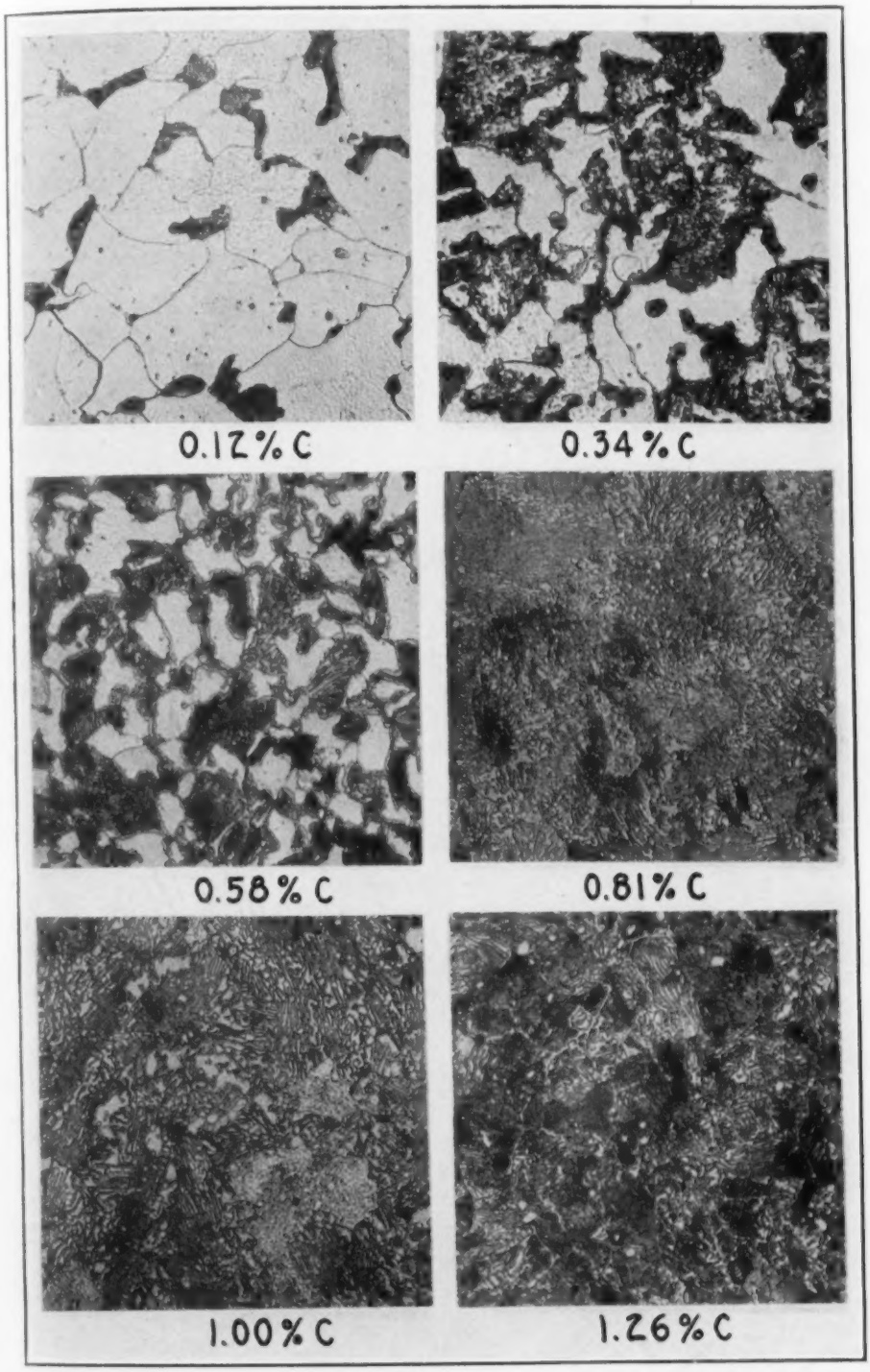

Fig. 7—Microstructures of the Normalized Steels, × 500. Etched with 2 per cent nitric acid in alcohol.

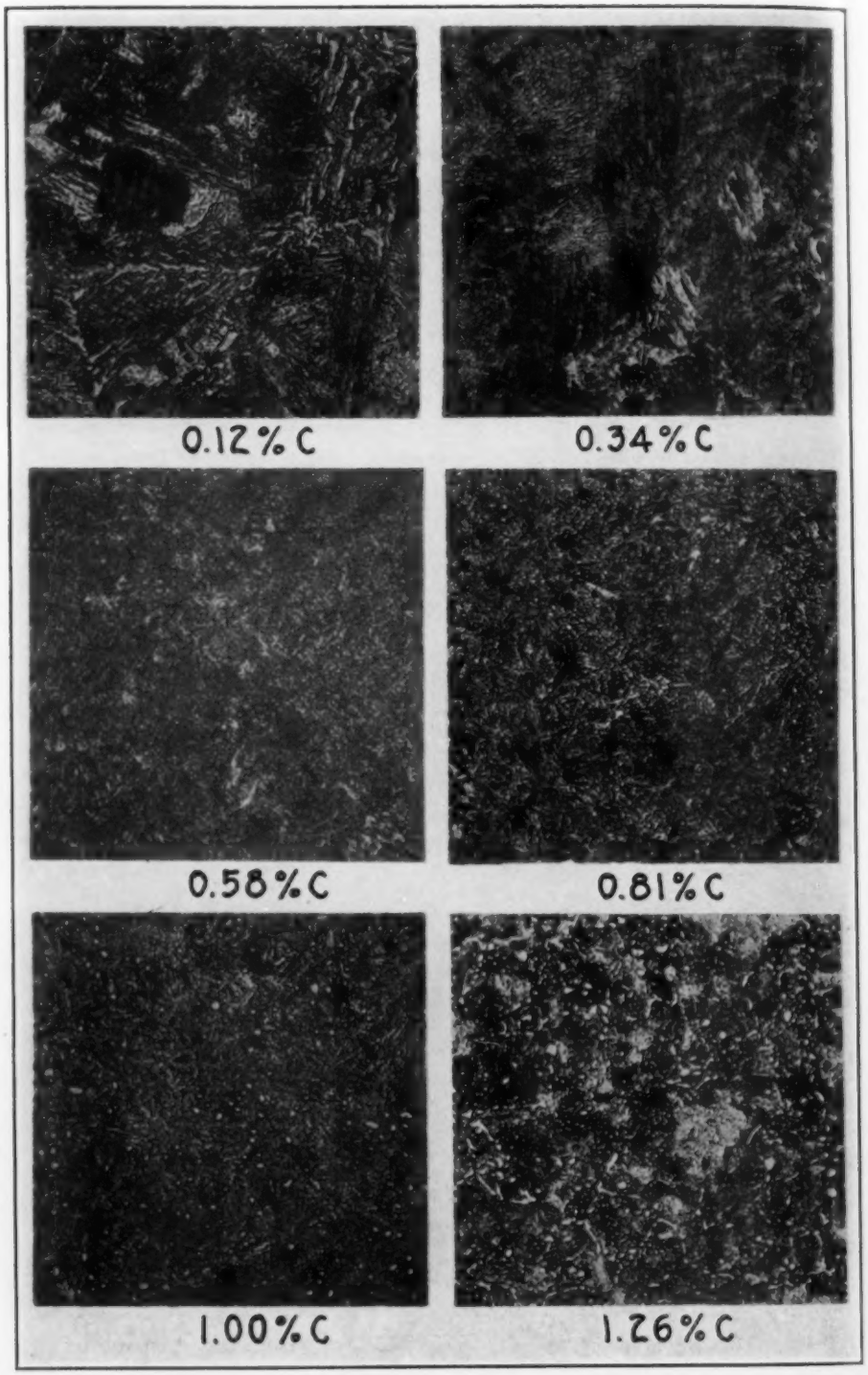

Fig. 8—Microstructures of the Hardened Steels, × 500. Etched with 2 per cent nitric acid in alcohol.

lowered the resistance to wear of eutectoid carbon steel as determined in the Amsler machine. See Fig. 10 for microstructures.

7. *Examination of the Abraded Surfaces*

A study was made of the structures of the steels adjacent to the

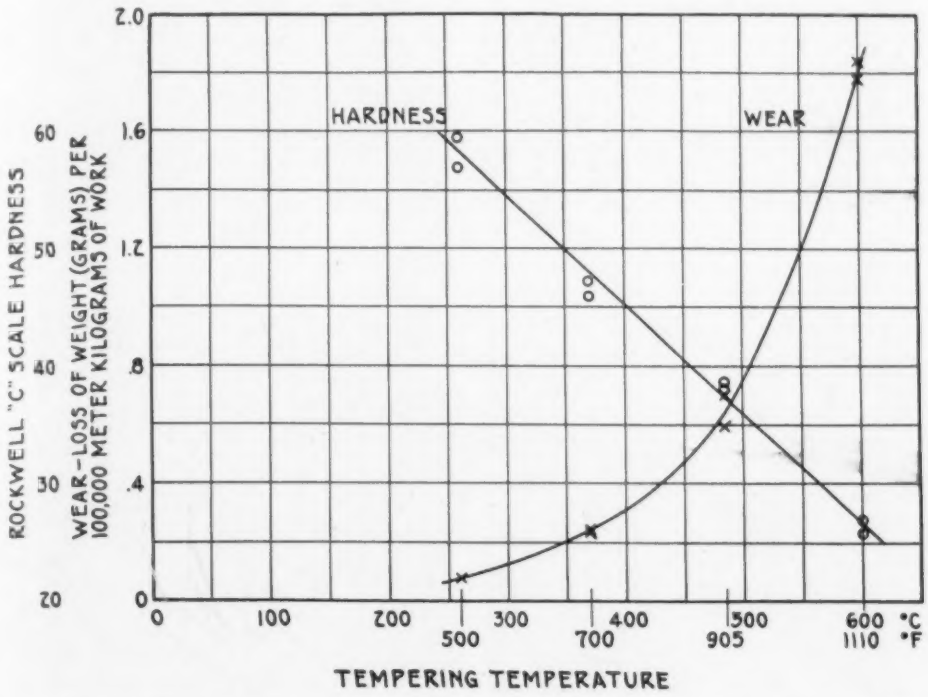

Fig. 9—Effect of Tempering Temperature on the Wear of an 0.81 per cent Carbon Steel.

worn surfaces. The appearance of these structures in the steels representing the lowest and highest carbon contents are shown in Fig. 11.

The low carbon steel showed marked distortion of the grains near the surface after wear in all conditions of heat treatment. The gradation from distorted to normal structure can be seen in the photomicrographs. The photomicrographs of the high carbon steel do not show any such gradation on the picture, but by comparing the structure near the surface with the corresponding normal structure shown in Figs. 6, 7, and 8, it can be seen that the entire layer of metal adjacent to the surface shown in the photomicrographs of the normalized and hardened steels was so severely distorted as to obliterate the base structure entirely. The structure of these two steels slightly below the worn surface could not be resolved under the mic-

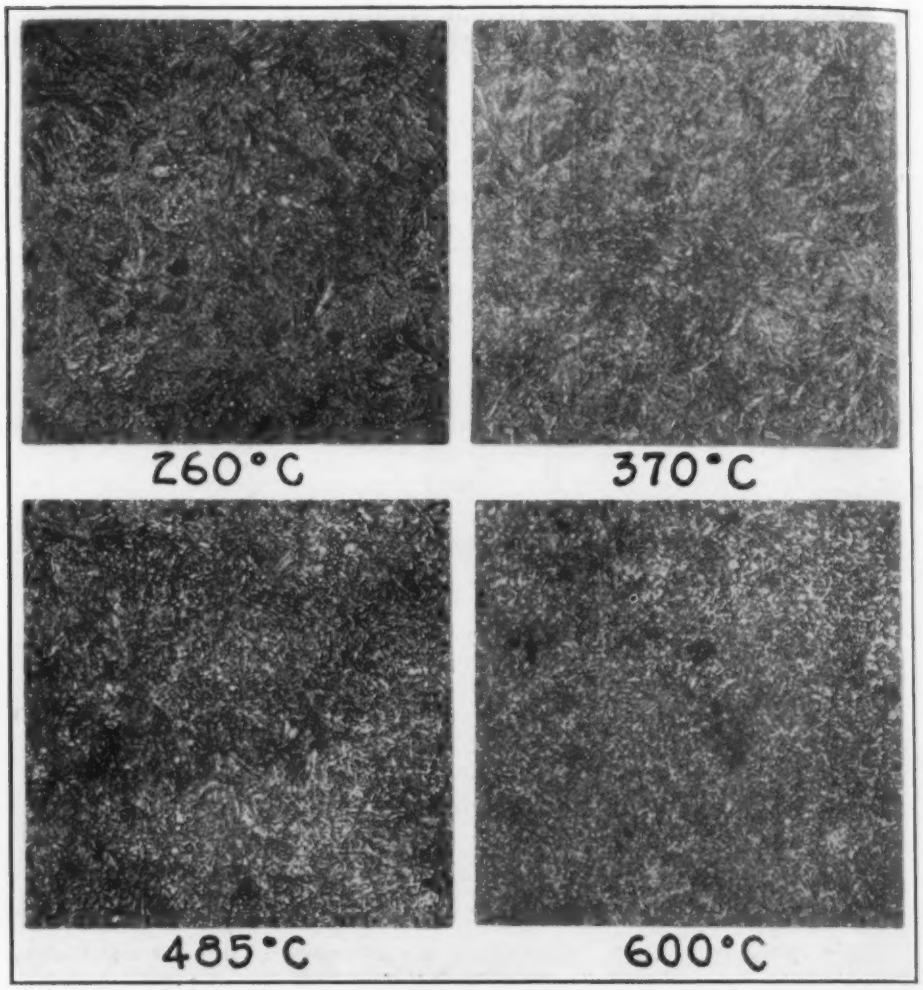

Fig. 10—Microstructures of the Tempered 0.81 per cent Carbon Steel, × 500. Etched with 2 per cent nitric acid in alcohol. Tempered at temperatures indicated.

roscope even when viewed at a magnification of 2000 diameters. The structure of the annealed high carbon steel slightly below the worn surface showed evidences of the carbide particles having been brought closer together, presumably by the distortion of the surface layers. Prolonged etching failed to reveal the ferrite boundaries adjacent to the surface. These boundaries were easily revealed at some distance below the surface.

Microscopic examination of the normalized 1.00 per cent carbon steel revealed some interesting and unusual features in the structure adjacent to the surface. At one point it was found that a distorted structure extended inward for some distance and, instead of

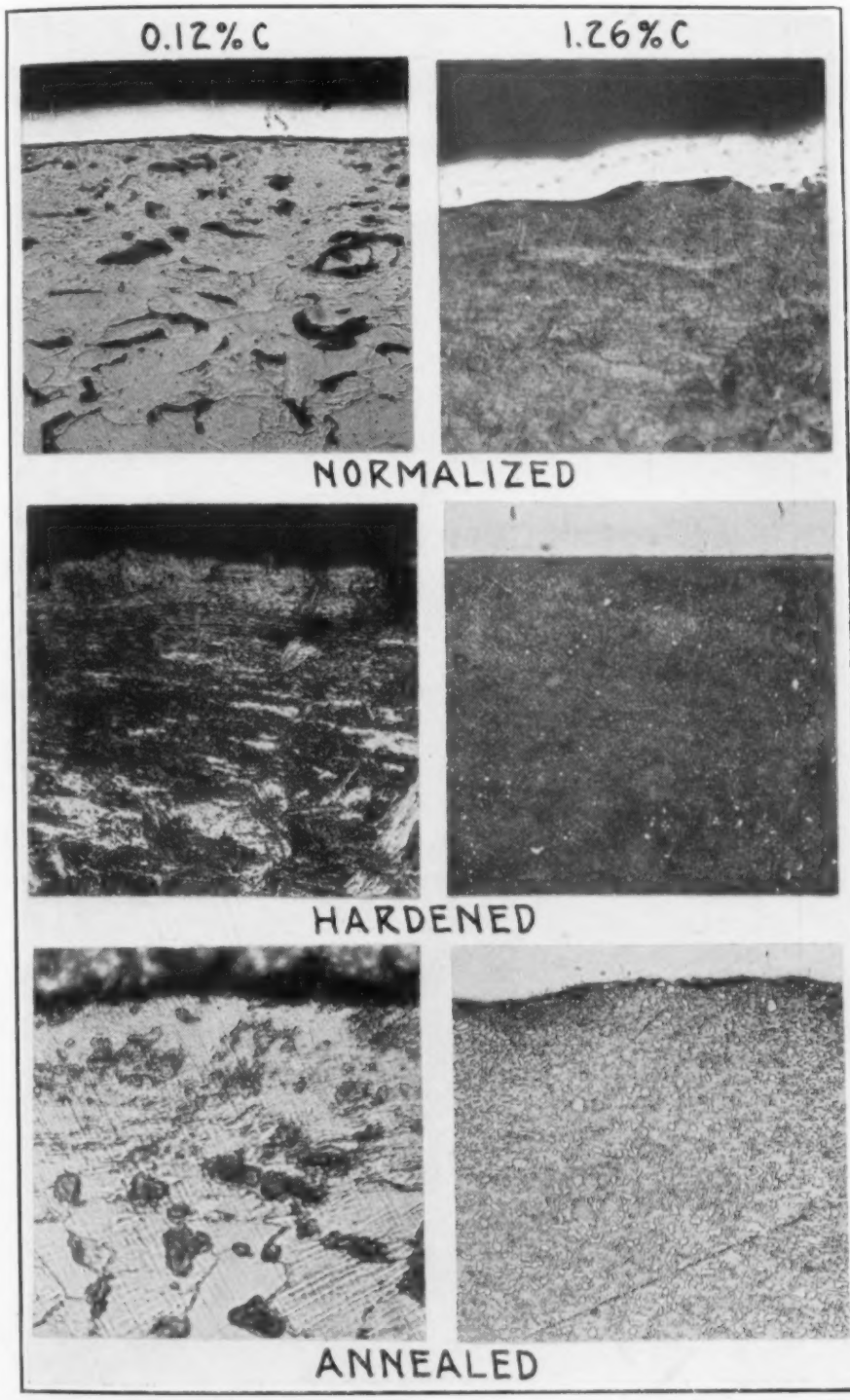

Fig. 11—Micrographs of the Structures Adjacent to the Worn Surface of the Low and High Carbon Steels Tested, × 500. Etched with 2 per cent nitric acid in alcohol.

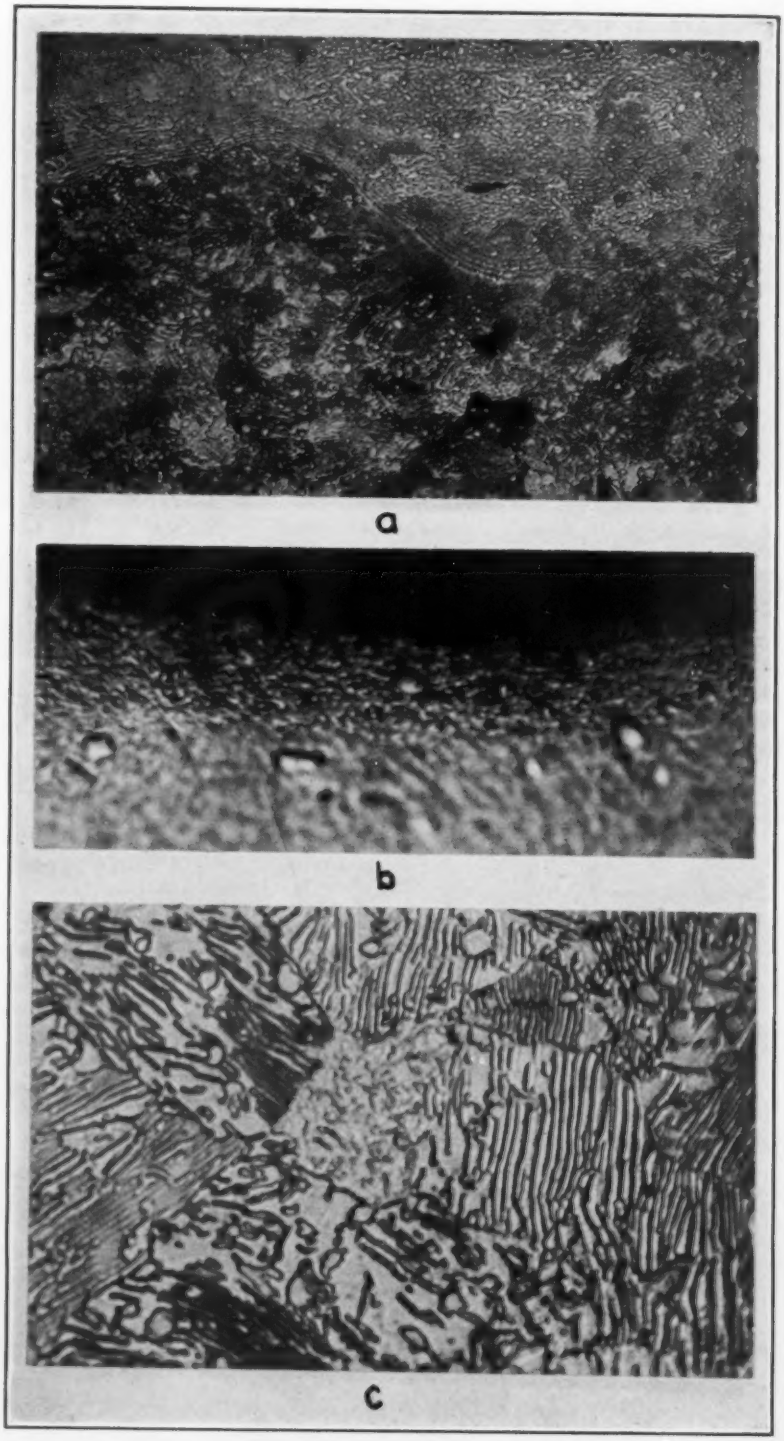

Fig. 12—Some Unusual Features in the Structure Adjacent to the Wearing Edge of a Normalized 1.00 per cent Carbon Steel. Etched with 2 per cent nitric acid in alcohol.

a. Micrograph Showing a Sharp Line of Demarcation Between Distorted and Normal Structure, × 500.

b. Micrograph Showing a Thin Layer of Severely Distorted Structure at the Wearing Surface, × 2000.

c. Normal Structure, × 2000.

merging gradually into the normal structure, was sharply separated from it by a wavy boundary. The appearance of this structure is shown in Fig. 12a.

At other points adjacent to the surface, the same specimen showed no definite evidences of distortion of the structure at 500 magnifications. At 2000 magnifications, however, a thin layer of severely distorted structure was found, as shown in Fig. 12b. The normal structure at 2000 magnifications is shown in Fig. 12c.

III. Discussion of Results

Despite the fact that the Amsler wear testing machine has many peculiarities, most of which are at best imperfectly understood, the results of the tests embodied in this report have shown that it is possible to secure consistent results with this machine. In order to secure comparable results on two or more materials it is necessary to standardize upon some sort of test conditions, and then, if sufficient care is taken in making the tests, reliable data should be obtained.

The interpretation of test results in terms of the application of materials for service should be attended by considerable discrimination. Attempts to predict the behavior of metals in service from wear-resistance data secured with the Amsler machine should be made only when the service conditions involve combined rolling and sliding friction under relatively heavy pressures of a type similar to that encountered in the Amsler machine. Results obtained by one method of investigation of wear usually cannot be applied to service conditions involving wear of a different kind.

It is a fact that in the minds of many engineers the terms hardness and wear-resistance are synonymous and this opinion is evidenced every time the specification for a part to resist wear calls for a hardened steel. Generally speaking, it is true that the harder the material, the better is its wear-resistance. In the case of the carbon steels reported in this paper, the high carbon steels showed a greater wear-resistance than the low carbon steels and the hardened steels showed a higher wear-resistance than the normalized steels, which, in turn, with the exception of the low carbon range, showed a higher wear-resistance than the annealed steels.

From a study of the data and the microstructures of the steels tested, it is evident that a martensitic, or rather a martensitic-troostitic structure is the most favorable for resisting wear of the type

studied. Although both the annealed and the normalized steels in the high carbon ranges are relatively soft as compared with the hardened steels, their resistance to wear varies widely. The normalized high carbon steels show a resistance to wear almost as great as that of the hardened high carbon steels, while the annealed high carbon steels show a relatively poor resistance to wear. The structures of these normalized and annealed high carbon steels vary markedly. They may be divided into two classes. The structures of the normalized steels are of lamellar pearlite, whereas those of the annealed steels are mostly spheroidized cementite and ferrite. This spheroidization was the result of the relatively slow cooling through the critical range undergone by the steels during the annealing treatment. From the curves shown in Fig. 5, it would seem that lamellar pearlite is quite resistant to wear. This is in accordance with results reported by Lehman.[5] In making wear tests on cast iron he found that the main factor which governed the resistance to wear of cast iron was the percentage of pearlite.

Evidently the presence of either free ferrite or free cementite (as spheroids) is detrimental to the wear-resistance of normalized carbon steels. That free ferrite is distinctly harmful is shown by the wear of the low carbon steels, all of which exhibited low resistance to wear. The microstructures of these steels (Fig. 7) show the normal amount of free ferrite.

In the high carbon range, the 1.00 per cent carbon steel, as normalized, showed a somewhat greater loss of weight than either the 0.81 per cent or the 1.26 per cent carbon steel (Fig. 5). From the microstructures of these steels (Fig. 7), it will be observed that the 1.00 per cent carbon steel shows relatively numerous patches of free cementite. The 1.26 per cent carbon steel, although containing, of course, more excess cementite than the 1.00 per cent carbon steel, has most of its excess cementite in the form of thin envelopes surrounding the pearlitic grains.

As previously mentioned, the normalized low carbon steels showed slightly less resistance to wear than the same steels when annealed. An examination of the photomicrographs of these steels (Figs. 6 and 7) revealed that the pearlite in the annealed steels was surrounded by cementitic envelopes. The normalized steels did not

[5]H. Lehman, "Wear Tests on Cast Iron," *Foundry Trade Journal*, p. 36, Jan. 13, 1927; p. 35, Feb. 24, 1927.

show this feature in their structures. These envelopes, being rather continuous and much stronger than the surrounding ferrite, are responsible for the wear-resistance of the low carbon annealed steels being greater than that of the same steels when normalized.

As would be expected, tempering a hardened steel resulted in a gradual lowering of its resistance to wear. It is interesting to note that the hardened 0.81 per cent carbon steel tempered at 600 degrees Cent. (1100 degrees Fahr.) showed practically the same resistance to wear as the same steel annealed. The microstructures of these two steels (Figs. 6 and 10) seem, upon first glance, to be quite different, but a closer examination reveals that the tempered steel shows distinct evidence of spheroidization.

The microstructures of the steels adjacent to the worn surfaces show that the type of wear studied in this report was generally accompanied by severe distortion of the structure. This suggests a reason for the detrimental effect of spheroidal cementite. It would appear that cementite occurring as spheroids is easier to dislodge under severe rubbing action than cementite which occurs in lamellar pearlite or as relatively thin, continuous envelopes surrounding pearlitic grains in hypereutectoid steels.

IV. Summary and Conclusions

The resistance to wear of a group of carbon steels was studied by means of the Amsler wear testing machine in which the material is subjected to combined rolling and sliding friction under heavy pressures. Annealed carbon steels gave relatively poor wear resisting qualities for all carbon contents. Normalized steels showed low wear-resistance in the low carbon range but had greatly improved wear-resistance in the high carbon range. The hardened steels showed low wear-resistance in the lowest carbon ranges but as the carbon content increased the wear-resistance increased very rapidly until about 0.6 per cent carbon. Above this percentage the wear-resistance increased very slowly. Tempering a hardened steel resulted in a gradual lowering of its wear-resistance.

A martensitic-troostitic structure was the most favorable for resisting wear of the type studied. Properly normalized high carbon steels, which showed a structure of lamellar pearlite, had almost as good wear-resistance as the hardened steels. Annealed high-carbon steels, showing a structure predominately spheroidized cementite,

had relatively poor resistance to wear. Apparently free ferrite or free cementite (as spheroids) is detrimental to the resistance to wear. Wear of the type studied usually resulted in marked distortion of the structure of the steel adjacent to the worn surface.

V. Acknowledgments

The author desires to express his grateful appreciation to Houston Babb, junior scientific aid, for his conscientious assistance in many of the tests.

DISCUSSION

Written Discussion: By Dr. R. L. Geruso, Bell Telephone Laboratories, New York City.

Any paper on the problem of wear is of great importance. For some unexplainable reason there appears to be a dearth of information on the fundamentals of wear, although its economic aspect alone should attract the attention of investigators.

Despite the fact that the author has investigated metal to metal wear under heavy pressures with sliding and rolling friction, it should be pointed out that the surface film characteristics of the "standard" determined in some degree the wear-resistance of the carbon steels tested. Two different materials used as "standards" possessing identical surface corrosion characteristics under the conditions of test would give results difficult to differentiate. It is granted that at the beginning of the test, before appreciable corrosion films have developed, variations in wear-resistance, if such exist, would be obtained. However, once sufficient quantities of these films have formed, differences in wear-resistance would be hard to detect. It is felt that greater thought and attention should be given to the corrosion film characteristics of various materials under the conditions of test, as it has been our experience, especially where light loads are operating, that the character of the surface films developed and its rate of formation is one very important factor in the intermittent wear of metals.

It was stated in an earlier section of this paper that in the case of steel wearing against steel, the films formed are supposed to be oxides of iron and that these oxides act as abrasives. It is suggested that an evaluation be made of the abrasive qualities of these oxide films which are subsequently "charged" into the surface of the standard specimens. Moreover, our experience with problems involving the wear of metal to metal under light loads has shown that the nature of the underlying metal, and the adherence of the surface films formed, have great bearing on the wear of metals.

Before definite laws can be established relating to the wear of various classes of materials, the fundamental causes governing the variations that occur should be understood. It is pleasing to see that the author has tried to relate the following factors in his problems of wear: nature and type of structure, chemical analysis, and heat treatments. It has been our contention that

a consideration of the nature and type of structure is more important than the chemical analysis, and that a correct understanding of the conditions of use is also a prime consideration.

The fact that a martensitic-troostitic structure is the most favorable for resisting wear under heavy loads with sliding and rolling friction is verified by actual experience. Such a structure imparts remarkable wear resisting qualities to our 12 per cent manganese steel. Certain nickel-chromium steels[1] that have lately been used for special installations where severe wear is encountered have also proven to be the equal or superior as wear-resisting material to our 12 per cent manganese steel. It may be that the excellent wear-resisting qualities of this steel are likewise due to a definite proportion of martensitic-troostitic structure.

Written Discussion: By D. E. Ackerman, research laboratory, International Nickel Company, Inc., Bayonne, N. J.

In his discussion of film formation, Mr. Rosenberg has referred to the work of Dr. Max Fink, who claimed that in the absence of oxidizing gases he had obtained no wear with steels which wore freely when tested in air. The possibility of an effect of this sort is of such importance that the writer decided to check Dr. Fink's results, but was prevented from doing so by the fact that Dr. Fink's original publication in the "Organ für die Fortschritte des Eisenbahnwesens" overlooked one of the desirable features of a scientific paper in that it did not describe the experimental conditions in sufficient detail to permit of their accurate reproduction by others. No description or adequate photographs of the gas cell were given; the rate of gas flow into the test cell, and sufficient details regarding the nitrogen purifying train to permit others to produce equally pure nitrogen, were among the other important details which were omitted.

Although aqueous solutions were used by Dr. Fink in removing oxygen from his gas, the effluent gas from the drying train was apparently not tested to insure its freedom from moisture. In my own Amsler tests on cast iron, I have found that a surprisingly small content of moisture, even in relatively high oxygen content test atmospheres, is sufficient to lubricate the disks excellently, and to reduce the wear rate to a very low value. It has also been my experience that reducing the oxygen content of the dry test atmosphere markedly increases the wear rate, for, under these conditions, compact, adherent, protective oxide and wear-product films form much less readily. It is, therefore, my opinion that the type of wear which may take place in a dry, oxygen-free atmosphere should be considered an open question until further studies of the subject become available.

The data obtained by Mr. Rosenberg are in qualitative agreement with the commonly held idea that, for a given condition of heat treatment, wear-resistance is increased by increasing the hardness; moreover, the data confirm the well-known fact that, for a given hardness, the rate of wear varies with the microstructure. The great effect of hardness on wearing quality is well demonstrated by the author's Fig. 9, and the fact that the wear-hardness relationship in this case follows no mathematical law might be considered con-

[1]Nickel Steel—International Nickel Company Bulletin No. 10.

firmatory evidence of the fact that hardness and microstructure are only two of the factors affecting wear. What sort of wear-tempering temperature curve would the author expect if both disks of 0.81 per cent carbon steel had been tempered at each of the temperatures given in Fig. 9? Data on the equilibrium torques attained in the tests would be of interest, as they would throw light on the frictional properties of the steels. Is there any relation between curves obtained by plotting equilibrium torque and hardness or wear against carbon content?

It should be pointed out that the results reported in the paper are largely dependent upon the test conditions which were arbitrarily selected. The rates of wear would probably have been different if a low carbon steel had been chosen as the standard, or if the 0.81 per cent carbon standard steel had been used in the annealed or normalized condition. Indeed, it is probable that the small effect of carbon content upon the wear of the annealed steels is due to the fact that in this condition the hardness difference between different steels was negligible as compared with the hardness difference between any given steel and the steel which was chosen as the standard.

It seems to me that in a series of tests of this sort the rate of wear of the standard disks by the test disks is quite as important as the rate of wear of the test disks themselves. In practice, the rate of wear of one part of a wearing system cannot be considered independently of that of the rest of the system. I hope the author, in his closure, will include the rates of wear of the standard specimens when used against each member of the series of test disks.

I am inclined to disagree with Mr. Rosenberg when he says the Amsler wear-testing machine has many peculiarities. I suspect that these "peculiarities" are actually the results of the operation of unidentified factors which affect wear, and whose effects become apparent only because the Amsler machine now makes it possible to keep the more obvious factors, such as load and specimen motion, under control. There are ample grounds for believing that such unidentified influences exist, and it would seem desirable to correct this condition before too much effort is devoted to the systematic determination of wear rates under conditions which may later be found to exclude some important component of wear, or which may render correlation of different sets of data difficult.

The author rightly stresses the fact that his data are applicable to the prediction of service life only in the case in which service conditions are identical with his laboratory conditions. Those not intimately associated with the study of the wear of metals will not appreciate the enormous difficulties involved in conducting laboratory tests under service conditions. The problem is complicated, as has been said, by the existence of unidentified factors which affect wear, and by the fact that small changes in some of the less easily controlled variables may effect great changes in the rates of wear. It is my opinion that the position which will ultimately be accorded the wear test will be of the same type as is now accorded the corrosion test; that is, the laboratory test will be used to indicate the general type of service in which a given alloy may be used to the best advantage, and to select from the whole group of alloys available the best ones for a given general type of service. The selection of a material for his specific installation will be made by the user after trial instal-

lations of the small number of alloys which the laboratory tests have shown to be best for the general type of wear of which his particular problem is a special case.

Oral Discussion

A. H. D'ARCAMBAL:[2] Users of tool steel are always much interested in any papers covering wear-resistance of various materials. Unfortunately, however, the results usually obtained by these various wear testing machines do not seem to bear out the results obtained in practice. I was speaking to Mr. Rosenberg this morning concerning the results obtained from the normalized 1.20 per cent carbon tool steel with a Rockwell hardness of B 105, this material showing as great wear-resistance as hardened carbon tool steel, 1.20 per cent carbon, with a Rockwell of C 60. We also noted that the 0.12 per cent carbon steel hardened and drawn to 500 degrees Fahr. possessed a Rockwell reading of C 32. This hardness is considerably greater than one usually obtains from steel of this composition quenched and drawn to 500 degrees Fahr. The author also stated that the wear-resistance seemed to be increased when cementite networks were present. In regard to carbon tool steel, cementite networks are extremely objectionable. If the material comes to us in the annealed condition with cementite network present and also from 80 to 100 per cent lamellar pearlite, we not only experience trouble machining as well as hardening this steel due to cracking and non-uniform size change, but we also find that tools such as taps made from annealed carbon tool steel with cementite networks present will chip after very short service. It is therefore the practice of the majority of tool steel manufacturers to specify annealed carbon tool steel almost completely spheroidized or with a maximum of 20 per cent lamellar pearlite present and with complete absence of cementite network.

H. G. KESHIAN:[3] I am much interested in this paper; because it deals with an important property of steels on which we have little information of practical value.

Mr. d'Arcambal stated that the existing methods of testing the wear-resistance of steel are not satisfactory and as an illustration he pointed to the results in Fig. 5 where the wear-resistance of normalized high carbon steel is near that of hardened high carbon steel, and said that if this is taken at its face value, normalized plug gages should last as long as the hardened plug gages. This of course, as Mr. d'Arcambal says, is not true. I think it goes to show that when speaking of wear one must definitely state the type of wear under consideration. For instance, we have the straight wear of a cold drawing die with considerable pressure, impact wear of a header die, rolling wear of a roller or ball bearing, and it is quite obvious that no single manner of wear testing can be applied to these different types of wear. An attempt to the contrary will surely result in contradictions. This point alone, perhaps, will explain some of the unsatisfactory features of some of the present wear testing methods.

It seems to me that further study has to be made of the precise effect of the condition of cementite in hardened steels upon its wearing properties, that

[2]Metallurgist, Pratt & Whitney Co., Hartford.

[3]Metallurgist, Chase Companies, Waterbury, Conn.

is, whether the carbides are in solution or out of solution. We have actually faced this problem in a practical way. We had some very hard high carbon steel cold drawing dies and we obtained some results that did not look very good. Then we wanted to get all the carbide first in solution by using considerably high hardening temperature. The results still did not look quite satisfactory. The reason for this, we thought, must be that we were eliminating the wear-promoting constituent, that is, the carbides. Then we wanted to have some free carbide and used much lower hardening temperature. The results were much better. We are not, however, satisfied that this is a conclusive proof on the condition of carbides as they affect the wear-resistance and are carrying further tests.

Another point of interest to me in this paper is the effect of carbon on the wear-resistance. Mr. Rosenberg finds that above 0.60 per cent carbon there is no straight line relation between carbon content and wear-resistance and particularly, increase in wear-resistance above 0.60 per cent carbon is very little. This has been our experience with straight carbon steel drawing dies made from steels with carbon varying from 0.80 to 1.25 per cent.

C. L. FREAR:[4] About three years ago we had occasion to make wear tests on a number of sample lots of steel. Actual production tests were made by running the samples as vertical thrust bearings, the spherical bearing surfaces having a radius of approximately one inch, the load on the bearing being 36 pounds and the speed of rotation 6500 revolutions per minute. Both wearing parts were of the same composition.

We found that annealed carbon tool steel containing about 1.10 per cent carbon when quenched in water from 1600 degrees Fahr., then tempered at 300-400 degrees Fahr. gave the best wearing qualities even though a new file would bite the surface.

It was further found that the wearing qualities were much improved by heating this material to 1650 degrees Fahr. and cooling in air before subjecting it to the above heat treatment. This fact and also the study of micrographs lead us to believe that the presence of spheroidized cementite was a distinct disadvantage where good wearing qualities were desired. We finally, therefore, purchased our steel annealed only sufficiently to give us desirable machining properties. Such spheroidized cementite as is present in this annealed material is in a finely divided state and is easily eliminated by the normalizing treatment.

Author's Closure

I wish to thank Mr. Ackerman for his thorough discussion. His remarks as to the effect of atmosphere upon wear-resistance are extremely interesting and I hope that his experimental data will be made available shortly. He refers to the formation, under certain conditions, of a protective oxide film upon the surfaces of the test specimens and states that in a dry, oxygen-poor atmosphere these protective films form less readily. It is doubtless true, that the film protects, in a measure, the surface upon which it forms, but it also tends to

[4]De Laval Separator Co., Poughkeepsie, N. Y.

abrade the surface with which it is in contact. Some tests made at the Bureau of Standards showed that when the surface films were removed mechanically the wear rates were noticeably lower than when no attempt was made to remove the films. Mr. Ackerman has undoubtedly observed the fact that the lower specimen in the Amsler machine usually forms a heavier film than the upper specimen. This film, then, while it may protect the lower specimen in some degree, exaggerates the wear upon the upper specimen. Iron oxide (Fe_2O_3) has a Moh's scratch hardness of about 5.5 to 6.5 and martensitic steels are softer than this as is evidenced by the fact that rouge is sometimes used for polishing steels.

With reference to Mr. Ackerman's question as to what sort of wear-tempering temperature curve would be expected if both disks of 0.81 per cent carbon steel had been tempered at each of the temperatures given in Fig. 9, I would hesitate to make a definite statement. The combinations of metals tested have an important and, quite frequently, a surprising influence upon the rate of wear. I will venture the opinion that the general form of the curve would be the same as that shown in Fig. 9. The relative values, however, might be quite different. With reference to the equilibrium torques obtained during the tests, these were fairly uniform for all the steels tested. The carbon content of the steels apparently has little, if any, influence upon the torque. It was noted, however, that the equilibrium torques of the hardened steels were slightly less than those of the normalized and of the annealed steels.

I do not believe that the very small effect of carbon content upon the wear of the annealed steels was due mainly to the fact that in this condition the hardness difference between different steels was negligible as compared with the hardness difference between any given steel and the hardened steel which was chosen as the standard. This same general situation exists in the normalized steels, yet the carbon content had a marked influence upon the wear of these steels. These curves point to the fact that the microstructures of the steels have a much greater influence than the hardness upon the wear.

Experimental curves of the wear of the standard specimens were plotted during the progress of the investigation. Due, in my opinion, principally to the fact that these "standard" specimens were the ones which formed the heavier films, the wear of these steels was quite erratic and no consistent relationship between the wear of these "standard" steels against the test steels could be obtained. It may be mentioned that the wear of these "standard" steels was always less than that of the test steels.

The "peculiarities" to which I referred when speaking of the Amsler machine consist mainly of the surface films which form during test. These films, it is known, affect markedly the wear test results. Since these films are a natural result of wear between two metallic surfaces, it seems logical not to attempt their removal during test. Although methods for controlling these films may be devised, it is questionable whether the results obtained are truly representative of the wear-resistance of the combination of materials tested. Furthermore, if the positions of the two test specimens in the machine are reversed the results obtained are quite different due to the fact that the relative films formed and the motions of the specimens are different.

Mr. Ackerman's general remarks upon the difficulties of wear testing can

be appreciated only by those who have attempted to make a careful study of this vexing problem. I feel that Mr. Ackerman's thoughtful discussion is a real contribution to the subject and hope that this question of wear will receive the attention it merits in the future.

The discussion submitted by Dr. Geruso is very pertinent. The idea that two different materials possessing identical surface corrosion characteristics would give results difficult to differentiate when used as standard specimens is intriguing but, to my mind, somewhat doubtful. The films formed are mainly, if not entirely, oxides of iron as is evidenced by the fact that they are magnetic and can be reduced by heating in an atmosphere of hydrogen. These films form rapidly, becoming apparent almost immediately after the test is started. Dr. Geruso has, however, struck a keynote in wear testing when he stated that greater thought and attention should be given to these surface films.

I am glad to note that Dr. Geruso agrees with me that the nature and type of structure may be more important than the chemical composition in determining the wear-resisting characteristics of metals.

Mr. d'Arcambal seems to neglect the fact that these test results refer to one special condition of test and he attempts to apply them to his own particular requirements. This is one thing that cannot be done with wear tests. A tensile test, for instance, is a tensile test—you get so much ultimate stress and this is true no matter how the test is made, but a wear test is quite different. Involving, as it does, so many variable factors, it is applicable only to one special condition of service, and the results which have been reported are applicable only to such service which involves the wear of steel against steel under heavy pressure and combined rolling and sliding friction. The same conditions do not exist when steel is used for cutting, and it is not surprising, therefore, that these results do not check exactly what he has observed.

With reference to the remarks by Mr. d'Arcambal that the curves in Fig. 5 show that the normalized high-carbon steels have about the same resistance to wear as the hardened steels, I wish to point out that there is a considerable difference in the wear-resistance of these steels. The actual loss in weight per 100,000 meter kilograms of work is 0.0205 grams for the hardened 1.29 per cent carbon steel as against 0.0805 grams for the same steel when normalized. Due to the large scale necessary on the drawing, these differences do not stand out very well.

As far as the hardness of the quenched 0.12 per cent carbon steel is concerned, it was not uniform. The point given on the curve is the average of twelve readings on two specimens. These readings varied from Rockwell C21 to C37 and gave an average reading of C31.5 for each specimen. Under the microscope, this steel showed marked evidence of strain hardening despite the fact that it had been drawn at 500 degrees Fahr.

It is pleasing to have the confirmatory remarks of Messrs. Keshian and Frear, especially with respect to the detrimental effect of spheroidal cementite. A minute examination of the structure adjacent to the wearing surface of the annealed 1.26 per cent carbon steel reveals that the carbide particles have been brought closer together, caused, presumably, by the distortion of the surface layers induced by the wearing action. These carbide particles are probably dislodged under the rubbing action and thus cause excessive wear.

FORMATION AND ELIMINATION OF NONMETALLIC INCLUSIONS IN THE ACID OPEN-HEARTH PROCESS

By C. H. Herty, Jr., and J. E. Jacobs

Abstract

The first section of this paper includes a general summary of the manufacture of acid open-hearth steel.

The second part of the paper contains a detailed study of the following:

1. The elimination of nonmetallic matter originating in the charge and from the furnace lining.

2. Oxidation of metal during working of the heat.

3. Deoxidation with ferrosilicon and ferromanganese and with special manganese-silicon alloys.

4. Elimination of silicates in the ladle.

Experimental results indicate that steel deoxidized with a manganese-silicon alloy with the proper ratio of manganese to silicon gives a much cleaner steel in the ladle than steel deoxidized with ferrosilicon and ferromanganese.

FOR the past five years, the United States Bureau of Mines, in cooperation with Carnegie Institute of Technology and the Metallurgical Advisory Board, has been engaged in the study of the physical chemistry of steel-making, with particular emphasis on the basic open-hearth process. In February, 1930, a cooperative agreement was made between the United States Bureau of Mines and the Heppenstall Co. of Pittsburgh, Pa., to study the acid open-hearth process, with particular emphasis on the oxidation and deoxidation of the steel made thereby. Such a study necessarily involves all phases of steel melting in the acid furnace.

Scope of the Investigation

At the outset of the investigation it was decided to study six major factors in the production of acid steel, and two grades of alloy

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steel of the following percentage analysis were chosen for the investigation:

Constituent	Grade 1	Grade 2
Carbon	0.28–0.33	0.52–0.57
Manganese	0.60–0.80	0.55–0.70
Silicon	0.20–0.30	0.20–0.30
Nickel	1.5 –2.0	1.5 –2.0
Chromium	0.60–0.80	0.60–0.80
Molybdenum	0.40–0.50	0.20–0.25
Vanadium	0.15+	0.15+
Phosphorus (max.)	0.040	0.040
Sulphur (max.)	0.040	0.040

The six factors to be studied were:

1. The elimination of nonmetallic matter originating in the charge and from the furnace lining.
2. Oxidation of the metal during the working of the heat.
3. Deoxidation with ferrosilicon and ferromanganese and with special manganese-silicon alloys.
4. Elimination of silicates in the ladle.
5. Segregation of nonmetallic matter in the ingot.
6. Slag-metal reactions.

The experimental work is being carried out in the 20-ton furnaces of the Heppenstall Co. The average weight of metal tapped is 57,000 pounds. The hearth is 18 feet long and 7 feet wide, and the furnace is oil-fired.

To date, the first four items have been studied in detail, and work is being carried out on items 5 and 6; and, also, in connection with item 6, a further study is being made of the oxidation of the metal (item 2). Inasmuch as the writers expect to publish the results of further work at a later date, and as most previous work on the acid furnace has been connected with slag-metal reactions, reference to some previous investigators will be omitted here.

General Summary of Acid Open-Hearth Practice

The acid open-hearth process has been reviewed in a number of textbooks and in articles in technical journals. The most complete article on this subject is by Rassbach,[1] who gives an excellent review of present-day acid-steel melting practice. In view of this fact, the

[1] H. P. Rassbach, "Acid Open-Hearth Steel," Transactions, American Society for Steel Treating, Vol. 15, 1929, p. 289.

writers give only a brief outline of this phase, and those interested are referred to Rassbach's paper for details.

The Charge

Only a trace of the phosphorus and none of the sulphur is eliminated in the acid open-hearth process. This necessitates a careful selection of the materials to be used in the charge, because the finished product may contain a slightly higher percentage of both of these elements than the average of the charge, due to melting losses and a possibility of pick-up of sulphur from the flame. As for the carbon content of the charge, this element is oxidized readily and is controlled according to the type of product to be made rather than any limitation of the furnace. A high percentage of manganese is desirable in the charge, because during the melting period a large part of it is oxidized and gives a clean slag. Frequently, spiegel or ferromanganese is charged to bring the percentage of manganese in the charge up to 1.0 per cent or more for this reason. As a rule, the charge is made up to contain about 0.75 per cent of silicon for the three following reasons:

1. The oxidation of silicon is an exothermic reaction and facilitates the melting of the charge.

2. A considerable amount of FeO is produced on melting from oxidation of the scrap by the flame and from the rust in the charge. If there is not sufficient silicon in the charge to take care of this FeO, the furnace banks will be badly attacked.

3. If the silicon did not use up this FeO in the charge the bath would melt down wild, and the carbon content of the bath would be below the percentage desired at melt-down.

The scrap used must be selected by inspection and with much care. It is difficult and almost impossible to obtain a representative sample of scrap for analysis. The size of the scrap is also of importance. Unless the proportion of pig iron is large, light scrap makes it difficult to get a full charge in the furnace. Also, light scrap is excessively oxidized in melting, decreases yield, makes it difficult to control the carbon at melt-down, in addition to a resultant excess of FeO attacking the furnace banks.

Condition of the Heat at Melt-Down

The length of time necessary to melt an all-cold charge varies

from 3 to 5 hours, depending upon several factors: (1) The higher the percentage of pig iron in the charge the more rapidly it can be melted; (2) a new, sharp working furnace will melt a charge much quicker than a furnace that is nearing the end of its campaign; (3) lastly, the type of fuel used and methods of combustion control govern to a great extent the rapidity of the melt-down period.

When the charge is melted, the bath contains an average of 0.15 to 0.25 per cent silicon and 0.15 to 0.30 per cent manganese. In addition, there is usually present 0.50 to 0.75 per cent carbon in excess of that required in the finished product. The following tabulation gives two typical slag analyses at melt-down:

Type of Heat	FeO*	MnO	SiO_2	CaO
0.55 C	19.72	23.60	54.88	0.74
0.30 C	26.44	19.53	51.40	0.46

*Total Fe given in terms of FeO.

Reactions for Elimination

Carbon is eliminated by reaction with iron oxide,

$$C + FeO \rightleftarrows CO + Fe.$$

However, before the carbon can be removed to any great extent the residual manganese and silicon must be reduced to a value below 0.10 per cent, because at higher contents of silicon and manganese the iron oxide content of the bath is too low to allow reaction with carbon to proceed. This is accomplished by the iron oxide resulting from oxidation during melting in the interval between melt-down and the first ore addition, by the following reactions:

$$Si + 2FeO \rightleftarrows SiO_2 + 2Fe,$$
$$Mn + FeO \rightleftarrows MnO + Fe.$$

The main purpose of this interval is to get up temperature in the furnace and have the bath as hot as possible, because this condition is necessary for properly working a heat.

Working the Heat

After the residual manganese and silicon have been reduced and the proper temperature has been attained, the steel is ready to be refined. There are arguments both pro and con as to the merits of using appreciable amounts of ore during the working period. The general practice in this country has been to use small amounts of ore, whereas in foreign countries, especially Sweden, the practice has been

to use large amounts of ore, even up to a short time before tapping. As soon as the ore addition has been made, a vigorous boil ensues, and the carbon content of the bath begins to drop rapidly. When the fracture test reveals that the carbon content is approaching that desired in the finished product, silicon and manganese are added to the bath in the form of ferrosilicon and ferromanganese. This addition prevents further oxidation of carbon by the iron oxide. After the report has come from the laboratory that the carbon is at the desired point, the various alloys are added at definite intervals, usualy about 10 minutes. After the final manganese addition the heat is held in the furnace about 15 minutes before tapping to make certain that all the alloys go into solution. The heat is then tapped.

There is a great difference of opinion as to the proper pouring conditions, which includes handling the metal in the ladle. The time that the ladle can be held depends on the size of the heat and the temperature of the metal going into the ladle. The larger the heat and the higher the temperature the longer the ladle can be held without danger of freezing up during pouring.

The question of pouring ingots has been reviewed in detail by Rassbach and will not be discussed here. In acid open-hearth operation it is advisable to make all deoxidizing additions in the furnace and as few as possible in the ladle. In contradistinction to basic open-hearth practice, the alloy losses are smaller in acid practice because the slag is so much less oxidizing toward the metal.

Experimental Methods Used

The procedure used in this investigation was to follow heats from the time the furnace was charged until the steel was poured into the ingots. The analysis of the charge was known from a previous knowledge of the materials charged. Metal and slag samples were taken at definite intervals until the time the heat was ready to be deoxidized, just before deoxidation, at definite intervals between deoxidation and tap, and metal samples were taken on the pouring platform. The iron oxide in the metal was determined by the aluminum method.[2] The visible nonmetallic content[3] of the steel

[2] C. H. Herty, Jr., J. M. Gaines, Jr., H. Freeman and M. W. Lightner, "A New Method for Determining Iron Oxide in Liquid Steel," Technical Publication No. 311, American Institute of Mining and Metallurgical Engineers, February, 1930, 13 pp.

[3] C. H. Herty, Jr., C. F. Christopher and R. W. Stewart, "The Physical Chemistry of Steel Making: Deoxidation with Silicon in the Basic Open-Hearth Process," Cooperative Bulletin 38, U. S. Bureau of Mines, Carnegie Institute of Technology, and the Metallurgical Advisory Board, February, 1930, pp. 25 to 29.

was determined by the inclusion-count method. The electrolytic method[4] was used on these samples, but due to alloy contamination the present method had to be revised to take care of this type of steel. The slag viscosities were taken by the inclined-plane method.[5]

Results of This Investigation

1. Elimination of Nonmetallic Matter Originating in the Charge and from the Furnace Lining

Due to the difference in opinion of various operators as to the amount of ore to be used during the working period, this investigation includes heats which were worked (1) with no ore addition; (2) with very small ore addition; and (3) with relatively large ore additions.

From a theoretical point of view it seems reasonable that a large ore addition should be most advisable. In the bath after the silicon has been oxidized are a large number of small glassy silicate particles. To aid in their transfer from the metal to the slag, some action must take place, and the most logical agent to produce this action, as a lime boil is impossible, is an ore boil. For this purpose, a large lump ore is the best because it causes a much more violent boil than the small ore. On heats which melt down low in silicon, a vigorous action commences as soon as the heat is melted. These heats require less ore to obtain the desired action than those melting down higher in silicon. The amount of ore to be added is therefore left to the judgment of the melter who can easily estimate the silicon content in the bath at time of melt-down.

In addition to the vigorous action in the bath, there is one more factor that facilitates the removal of these silicate particles, and that is a fluxing agent. As the rising velocity of a particle of nonmetallic matter in the steel bath is proportional to the square of its diameter, the larger the particle the more rapidly it will rise out of the steel bath and enter the slag. For this reason it would seem advisable that some oxide such as MnO be formed in the bath at the time of the ore addition. The oxides SiO_2, MnO, and possibly some

[4]Cooperative investigation in progress.

[5]C. H. Herty, Jr., F. A. Hartgen, et al, "Temperature-Viscosity Relations in the System CaO-SiO_2"; Cooperative Bulletin 47, U. S. Bureau of Mines, Carnegie Institute of Technology, and the Metallurgical Advisory Board, October, 1930, 28 pp.

C. H. Herty, Jr., "The Diffusion of Iron Oxide from Slag to Metal in the Open-Hearth Process," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1929, pp. 284 to 299.

FeO would then combine, form large globules, and have a much greater tendency to rise to the slag during the boil than would the small SiO_2 particles alone. Following this line of reasoning, a spiegel addition of approximately 50 per cent of the weight of the ore is added to the bath just before adding the ore. Part of the manganese in the spiegel forms MnO in the bath when the ore is added and acts as the fluxing agent.

The following tabulation shows the percentage reduction in nonmetallic content of heats worked with ore and with ore and spiegel:

	Heats with ore alone	Heats with ore and spiegel
Before ore addition	0.008	0.006
One hour later	0.003	Less than 0.001

The advantage of using ore and spiegel is clearly shown and, as a matter of fact, on two of the heats worked with ore and spiegel there was no visible nonmetallic matter one hour after the ore addition.

About 1 to 1½ hours after the ore addition, the steel begins to "dirty up" again. Fig. 1 gives an example of the pick-up of nonmetallic matter from this time until the steel is ready to be deoxidized. It will be noted that the curve shows a maximum and that the heat is cleaning up at the time of deoxidation. From all indications it would seem that this increase in nonmetallic matter comes from bottom materials.

The types of inclusions are exceptionally small and very high in silica, and as there is very little silicon in the bath which can be oxidized to SiO_2, it seems impossible that this material could come from that source. This would indicate that the various grades of sand used for bottom material and the various methods of burning in the bottom materially affect the cleanliness of the steel during the working period.

The following tabulation shows the percentage of nonmetallic matter before this pick-up begins and the nonmetallic content just before deoxidation. This well illustrates the importance of using proper bottom materials.

Before SiO_2 pick-up from bottom begins	0.002 per cent
Silicate content just before deoxidation	0.005 per cent

There was considerable variation in the total amount of nonmetallic matter picked up. The nonmetallic content—0.005—is the average of seven heats. The dirtiest heat contained 0.016 and the cleanest 0.001 per cent silicates.

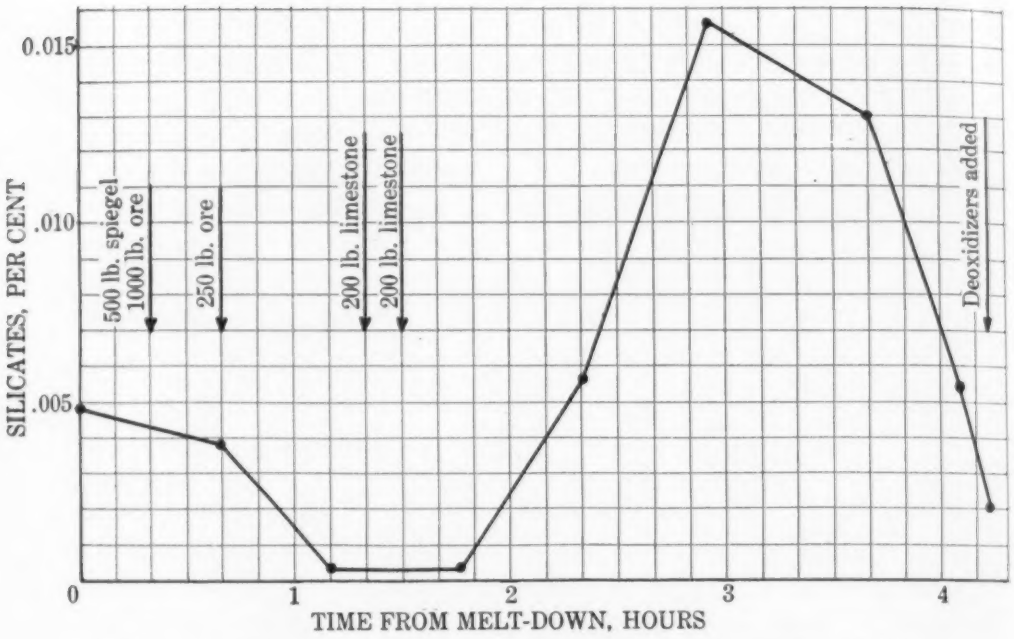

Fig. 1—Silicate Content of Acid Open-Hearth Bath During Working Period.

2. Oxidation of the Metal During Working of the Heat

Numerous data showing the oxidation of the steel in basic open-hearth furnaces have been published by one of the writers in connection with the work on the physical chemistry of steel-making mentioned at the beginning of this article. To the best of our knowledge, only one oxidation curve has ever been given for acid open-hearth work. One of the essential factors of this investigation was therefore a study of the oxidation of the bath and the factors controlling it. On all the heats, iron oxide in the metal was determined by the aluminum method, and the curves for the two grades of steel studied and for one heat of low-carbon steel[2] are shown in Fig. 2. The oxidation curves for the 0.55 and 0.30 per cent carbon grades have been corrected for visible nonmetallic matter, whereas the oxidation curve for the low-carbon heat has not been so corrected. However, the corrections are small enough on the higher carbon steels that they amount to very little on the high iron oxide of the low-carbon steel heat. As would be expected, the oxidation of the heat increases as the carbon drops, although this is not as pronounced on the high carbons as on the low-carbon heat. The factors affecting the oxidation of the metal are (1) the carbon content; (2)

the slag composition; (3) the slag viscosity; and (4) the temperature. The oxidation of the metal at 0.30 and 0.55 per cent carbon on the low-carbon heat is greater than on the higher carbon grades because the slag was kept much more highly oxidizing so that the heat could be brought down to 0.12 per cent carbon as rapidly as possible.

In basic open-hearth practice the iron oxide content of the metal very seldom decreases unless a deoxidizer is added. On the other hand, in acid operation such a drop has been noted before the addition of the deoxidizers. This drop is caused by the change in slag composition and viscosity. As the slag picks up more and more silica from the furnace lining, the free iron oxide content decreases and the viscosity of the slag increases. Both of these factors tend to decrease the rate of diffusion of iron oxide from slag to metal, and as the carbon reaction is proceeding at all times, there is necessarily either a decrease in the rate of pick-up of iron oxide or an actual decrease in the iron oxide content of the bath. The average iron oxide content of the metal before deoxidation was 0.054 per cent for nine heats of the 0.55 per cent carbon grade and 0.076 per cent for three heats of the 0.30 carbon grade. The single heat of 0.12 per cent carbon steel showed 0.17 per cent iron oxide. As the carbon drops, there is more and more iron oxide to be deoxidized, which, with normal deoxidation practice, would result in more and more nonmetallic matter in the final product. It will be noted, however, that the change from the low-carbon steel to the 0.30 per cent carbon steel is more pronounced than the change from the 0.30 to the 0.55 per cent carbon steel—a fact which is in accord with theory and which has also been noted in basic open-hearth work.

3. Deoxidation with Ferrosilicon and Ferromanganese and with Special Manganese-Silicon Alloys

Before discussing deoxidation, it is necessary to remark on the condition of the slag throughout the heat. As mentioned previously, slag viscosities were measured by the inclined-plane method, [3, 5] which is operated as follows:

> The viscosimeter consists of a steel plate 51 inches long and 6 inches wide bent to give a 6-inch horizontal section, and a 30-inch section inclined 30 degrees to the horizontal. This is set up directly in front of the wicket hole. A spoonful of slag is taken from the furnace, the spoon rested on the horizontal section, and then turned quickly so that the slag runs down the

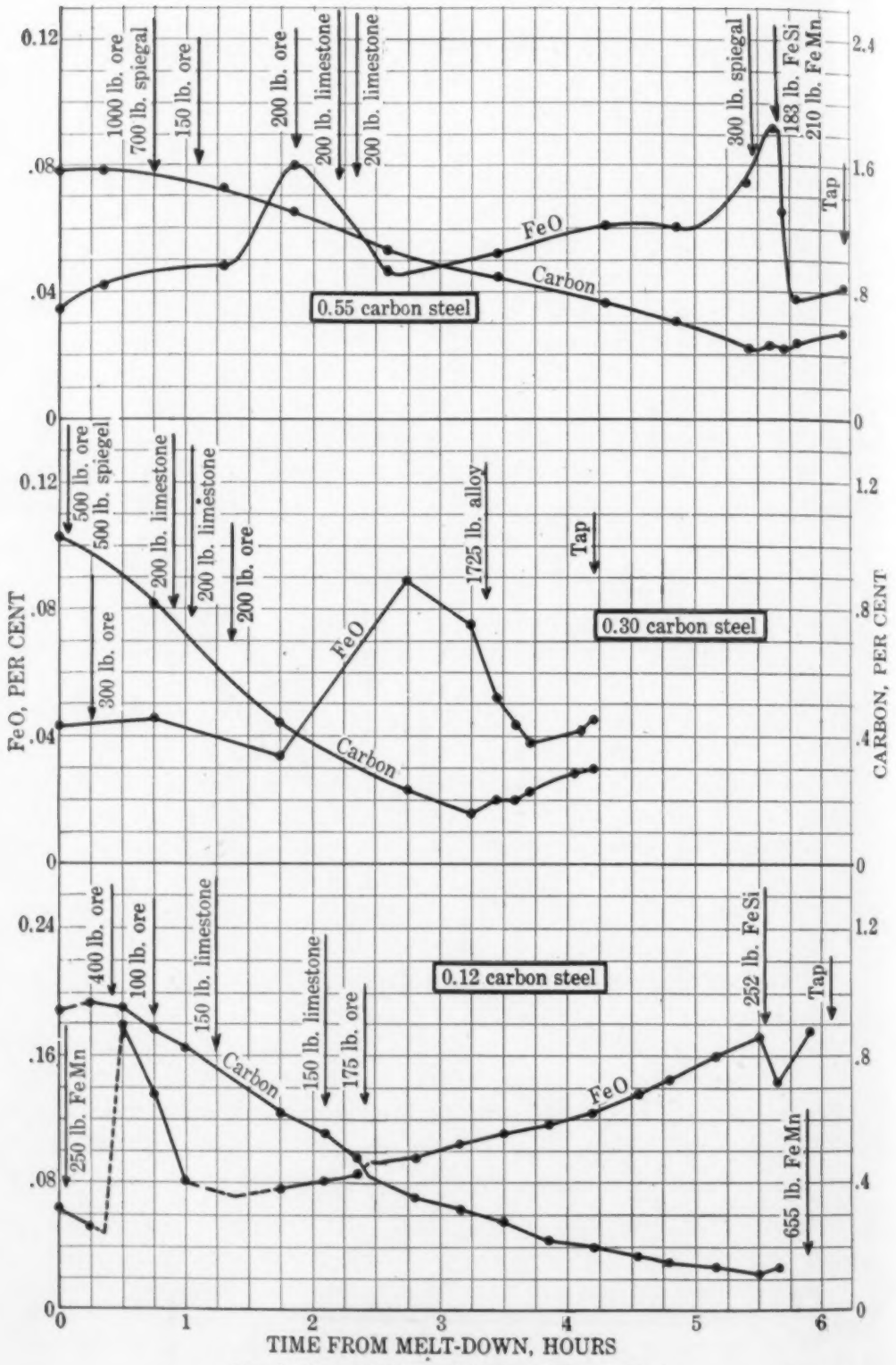

Fig. 2—Iron Oxide in Acid Open-Hearth Steel.

plane. The slag freezes on the plane. The thickness of the slag at an arbitrarily chosen point 6 to 10 inches from the horizontal section is measured with a pair of micrometers reading in millimeters. This thickness has been found to be a direct indicator of the true viscosity of the slag.

Not much is to be done to control the slag viscosity until about an hour after the ore addition. The increase in the FeO content due to the ore addition causes the slag to be very thin and watery during this interval. It is very important that the slag have the proper viscosity when the heat is ready for deoxidation. If the slag contains only silica, iron oxide and manganese oxide, there is a very sharp change in viscosity at 56 to 58 per cent silica. On the other hand, if lime is added to such a slag the change in viscosity is not so sharp and the viscosity is more easily regulated. Hence, after the ore has worked through the bath, 200 to 400 pounds of limestone is added to the slag, depending upon its condition at that time. From then on until the heat is tapped, the viscosity is watched very closely, for great care must be taken to see that the slag does not become too heavy or viscous, because if this happens the nonmetallic matter in the bath at this time and also the products of deoxidation do not have much chance of entering this type of slag. Moreover, a heat tapped with a heavy viscous slag over it usually shows a "kick-back" of inclusions in the ladle. By this is meant that the nonmetallic content of the steel after tapping is higher than the nonmetallic content of the steel in the furnace just before tapping. Thus, before any final additions are made to the heat, if the slag has a tendency to become heavy and viscous, a few shovels of fine ore dust, manganese dust, or scale are scattered over it until it reaches the desired viscosity. Burnt lime may be used at this time, but its action is much slower than the materials mentioned.

If the slag has been worked properly, the only danger which the operator faces is that it may become too heavy through excessive erosion of the furnace lining. However, if the slag should be too thin before deoxidation, which is not probable, it may be thickened by dropping the temperature slightly or by adding silica sand.

The following tabulation shows the average slag and metal compositions which were found in this work just prior to deoxidation:

	Slag				Metal		
Grade	FeO	MnO	SiO_2	CaO	C	Mn	Si
0.55 C	15.66	20.79	55.00	4.88	0.49	0.17	0.10
0.30 C	18.88	18.14	55.10	4.12	0.17	0.10	0.08

The average slag analysis for the 0.55 per cent carbon grade includes the heats deoxidized with ferrosilicon and ferromanganese, and with the manganese-silicon alloy, because the slag analyses were essentially the same for both types of heats. However, the heats deoxidized with the alloy were killed at 0.45 per cent carbon instead of 0.49 per cent on account of the carbon content of the alloy. On the 0.30 per cent carbon grade the carbon content is lower at deoxidation than would normally be expected for the same reason—that is, the carbon content of the alloy is greater than the carbon content of ferrosilicon plus ferromanganese.

From the tabulation on page 281 is shown that slags on the lower carbon heats contained more FeO and less MnO than the slag on the higher carbon heats, this being a natural result of oxidation by the furnace gases. Similarly, and following the discussion of oxidation of the metal, the manganese and silicon content of the metal is lower on the lower carbon grade of steel.

If the reaction $FeO + C \rightleftarrows CO + Fe$ is allowed to proceed indefinitely, the carbon content of the steel will fall to a very low value. Simultaneously, as the amount of carbon in the steel decreases, the amount of iron oxide increases. Consequently, if steps were not taken to stop this reaction, it would be difficult to meet the imposed chemical specification for the finished product. If the FeO content of the steel was not reduced, the metal after solidification would contain large gas holes caused by the evolution of CO gas.

For these reasons, after the carbon in the metal has been lowered to a point near the finishing specification, either the heat is "tied up" so that the excess SiO_2 in the slag is reduced, causing a pick-up of silicon in the metal, or deoxidizers are added to the bath to react with the FeO and prevent further reduction of the carbon by forming more stable oxides, which are practically insoluble in steel and are only slightly reduced by carbon.

The first mentioned method of finishing a heat, namely, "tying it up," is one which is used without knowledge of what actually happens during this period. Yaneske[6] states that he believes the following reaction takes place between iron and the excess SiO_2 in the slag above that required to satisfy the basic oxides:

$$SiO_2 + Fe \rightleftarrows FeSi + O_2.$$

[6]B. Yaneske, "Deoxidation and the Influence of Lime on Equilibrium in the Acid Open-Hearth Furnace," *Journal*, Iron and Steel Institute, Vol. 99, No. 1, 1919, pp. 255 to 270.

If this is true, this excess SiO_2 is reduced by the iron, and the oxygen liberated from the SiO_2 perforates the metal. In the furnace bath where the slag is only in contact with the surface of the molten metal, the oxygen liberated will pass off as nascent oxygen. In a discussion of a paper by DeMare,[7] Ball agrees with Yaneske that the reduction of SiO_2 is caused by the reaction with iron.

DeMare disagrees with the theory put forth by Yaneske and Ball. He believes that with steadily increasing temperature the oxidation of Si is first checked, then held, and finally, due to the high temperature and the large excess of SiO_2 in the slag above that necessary to combine with the basic oxides, the affinity of C for O_2 has increased to the point where it will reduce the Si out of the SiO_2 according to the reaction $2C + SiO_2 \rightleftarrows Si + 2CO$. This leaves the Si free in its nascent state to deoxidize the steel, as shown by the increasing solidity and freedom from blowholes of the subsequent tests. J. E. Stead holds this view in discussing McWilliams and Hatfield.[8]

From reviews of the present literature it is readily seen that there are two general theories as to what actually happens, but few experimental data are available. However, considering the reaction $SiO_2 + 2Fe \rightleftarrows Si + 2FeO$, it is a known fact that this reversible reaction actually takes place at steel-making temperatures. As the temperature increases, the per cent of SiO_2 in the slag increases while the per cent of FeO decreases. This means that the silicon content of the metal must increase. Also, since the reaction $2C + SiO_2 \rightleftarrows Si + 2CO$ takes place at very high temperatures, it is quite probable that this reaction is beginning to take place at steel-making temperatures. Both reactions are possible and there is every reason to believe that both operate simultaneously, as high temperatures favor the reduction of silicon by each reaction. The present investigation will include a detailed study of this phase of the process, and the results will be published later.

To the present time, the part of the investigation dealing with deoxidation has been confined to the addition of deoxidizers and has not included a detailed study of the two reactions discussed.

The first heats made were deoxidized in the furnace with 50 per cent ferrosilicon and ferromanganese. The formation and partial

[7] B. De Mare, "The Acid Open-Hearth Process," *Blast Furnace and Steel Plant*, Vol. 8, June, 1920, pp. 318 to 324; 385.

[8] A. McWilliams and W. H. Hatfield, "The Elimination of Silicon in the Acid-Open Hearth," *Journal*, Iron and Steel Institute, No. 1, 1902, pp. 54 to 69.

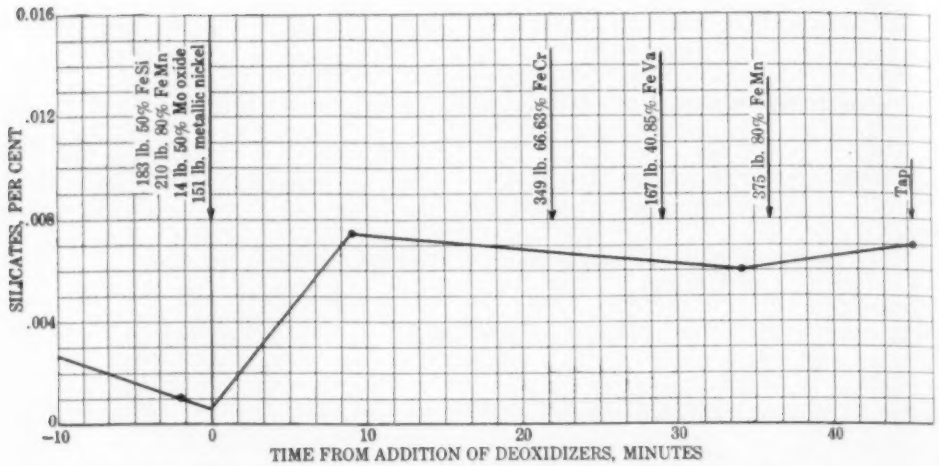

Fig. 3—Elimination of Silicates After Deoxidation with Ferrosilicon and Ferromanganese in 0.55 Per Cent Carbon Steel.

elimination of the oxides formed are shown in Fig. 3. This curve shows that there was a considerable amount of nonmetallic matter left in the steel when the heat was ready to be tapped. The maximum amount present was probably not observed because too much time was allowed between the addition of the deoxidizer and the taking of the first sample. On other heats, as shown later, samples taken immediately after the addition had a higher nonmetallic content than shown in this curve. Oftentimes the maximum dirtiness of the steel has not been reached until just before tapping time. This allows very little time for any cleaning action to take place in the furnace; consequently, the finished steel contains an appreciable amount of nonmetallic inclusions.

Later, 11 heats were made which were deoxidized in the furnace with an alloy developed at the U. S. Bureau of Mines in connection with the program on the physical chemistry of steel-making. This alloy contained approximately 31 per cent manganese, 4.9 per cent silicon, and 2.4 per cent carbon. The amount of alloy to be added varies with the grade of steel to be made, but in general about 0.15 per cent silicon is added in the form of the alloy. Fig. 4 shows the elimination of silicates on the two grades of steel deoxidized with this alloy which has a lower melting point than ferromanganese and ferrosilicon separately, and goes into solution much more readily, killing the heat almost instantly. The types of inclusions formed are much larger than those with ferromanganese and ferrosilicon and rise out of the bath with surprising rapidity.

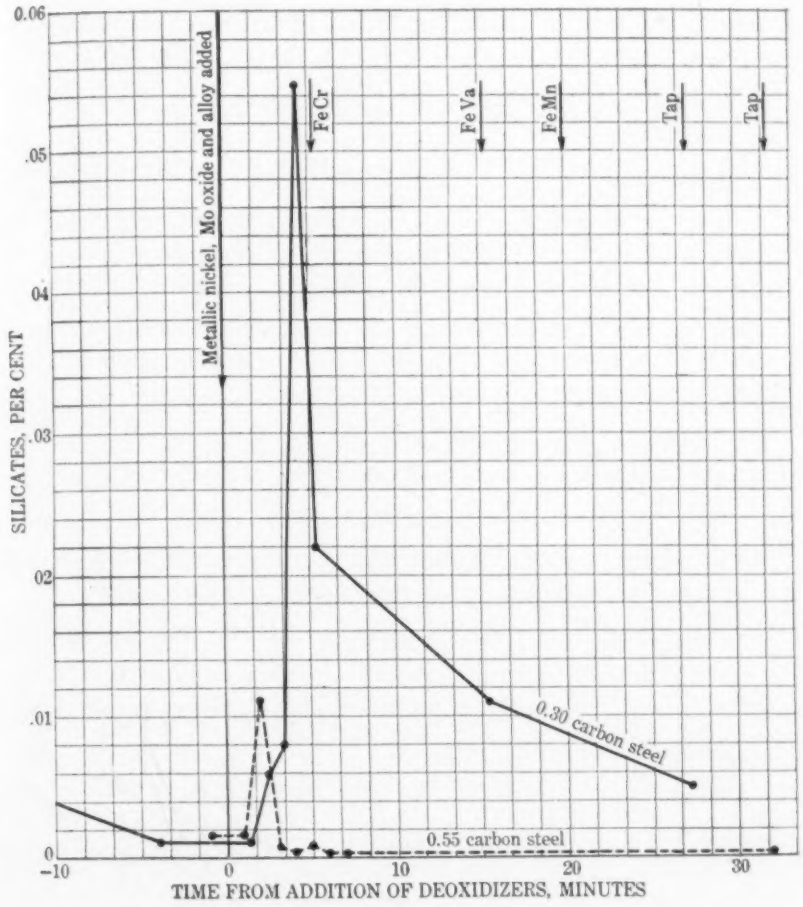

Fig. 4—Elimination of Silicates After Deoxidation with Manganese-Silicon Alloy.

resulting in a very clean steel within a few minutes after the deoxidation. From this time on to tap, the smaller particles which have not risen out of the bath have an opportunity to do so. The net result is that the tapping tests are very much cleaner when the steel is deoxidized with the manganese-silicon alloy than when deoxidized with ferromanganese and ferrosilicon. The average silicate content in the tapping tests of the heats deoxidized with ferrosilicon and ferromanganese was 0.010 per cent. In the heats deoxidized with the alloy it was less than 0.001 per cent; these data are on steel of the 0.55 per cent carbon grade.

As the investigation proceeded it was found advisable to add about 0.40 per cent of manganese, as ferromanganese, to the bath about 10 minutes before tapping. This seems to aid materially in cleaning the bath of residual oxides.

It should be noted here that the use of the alloy followed by manganese results in a steel which is clean not only of deoxidation products, but of any oxides which come from the charge or from the furnace bottom.

The finishing slag has a considerable influence on the cleanliness of the steel in the ladle. If the slag is extremely viscous in the furnace, proper absorption of nonmetallic matter does not take place, with the result that when the heat is tapped the nonmetallic matter floating just under the slag surface is mixed with the remainder of the metal, the net result being a dirtier steel in the ladle than was observed from furnace tests. However, if the slag is of proper consistency, a viscosity of 4.0 to 4.5 millimeters by the inclined-plane method, no such kick-back occurs because such a slag will readily absorb nonmetallic matter from the bath. This is clearly brought out by grouping the change in nonmetallic content between the tapping tests and the ladle tests according to the viscosity of the finishing slag. Below is shown the change in nonmetallic content according to this grouping. A positive number indicates an increase in silicate content from tapping test to ladle test, a negative number indicates a decrease:

Slag viscosity, mm.	Change in per cent silicates
6.0	+0.007
5.0	+0.001
4.5	−0.012
4.0	−0.002
3.5	−0.001

It is of the utmost importance, therefore, in making high-quality steel, to avoid a very viscous slag during the finishing period of the heat. This is particularly true when using the manganese-silicon alloy, because the function of the alloy is to give large inclusions which will rise out of the bath readily, and if the slag is too heavy these inclusions will be thrown back into the steel and will result in large particles in the finished product.

4. Elimination of Silicates in the Ladle

After the steel has been tapped into the ladle, if the temperature permits, the ladle is held 20 minutes before the pour is started. While the steel is being held in the ladle, some of the inclusions which have not been eliminated prior to tapping have a chance to coalesce and rise up to the slag-metal surface. Fig. 5 brings this

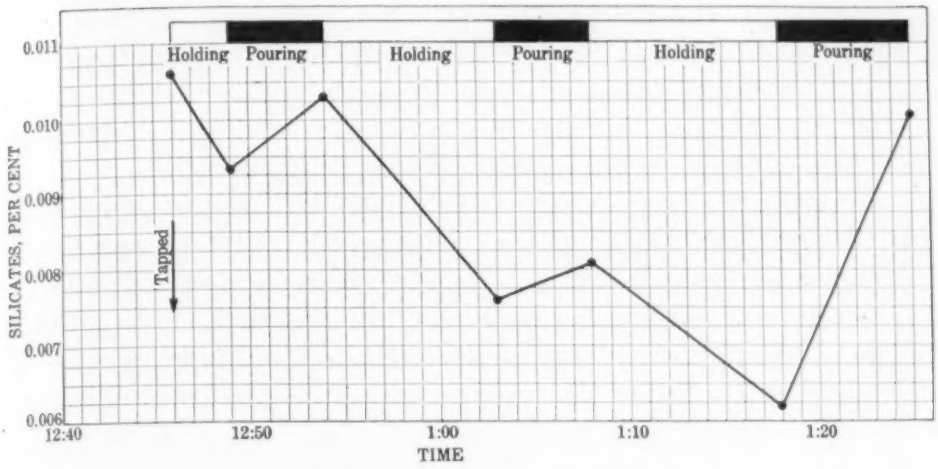

Fig. 5—Elimination of Silicates During Pouring.

out clearly.[9] (The inclusion content of the steel for this curve was determined by the Dickenson method.[3]) The silicate content of the steel shows a decrease immediately after tapping. While the first ingot was being poured, the level of the steel in the ladle dropped, and the inclusions were overtaken in their ascent. Similarly, during the second and third holding and pouring periods, the same drop and rise in nonmetallic matter was observed. The reason for this marked rise during the last pouring period is that this sample represented the last metal poured and was very close to the slag surface. This curve shows the advantage of holding the ladle before starting to pour.

This investigation goes only as far as the ingot. To date no work has been completed on solidification phenomena, segregation, or reactions which take place after the steel has been poured into the ingot. This work is under way at the present time, and when completed a second paper will be written dealing with these subjects, in addition to giving specific data on slag-metal reactions.

Summary and Conclusions

The following conclusions may be drawn from this investigation:

1. There is present in the bath at the time the heat is ready to be ored a considerable amount of nonmetallic matter originating from the charge and from the oxidation of silicon. This non-

[9]Unpublished Bureau of Mines report by C. H. Herty, Jr., and J. M. Gaines, Jr.

metallic matter is eliminated to a certain extent by the action of the ore, but it has been found that the addition of spiegel with the ore facilitates the removal of these impurities.

2. In the furnace under investigation, a pick-up of silica was noted during the working period and was attributed to material coming off the bottom. After a high enough temperature is reached, most of this nonmetallic matter is eliminated by the boiling action in the furnace. The use of the manganese-silicon alloy followed by a small manganese addition apparently eliminated inclusions from the above source, as well as the normal products of deoxidation.

3. The iron oxide content of acid open-hearth steel increases gradually as the carbon is eliminated. Toward the end of the working period the iron oxide content of the metal may hold constant or decrease, even though the carbon is dropping, due to changes in slag composition, slag viscosity, and temperature.

4. Deoxidation with manganese-silicon alloys gives a much cleaner steel in the furnace than deoxidation with ferromanganese and ferrosilicon. The alloy works much more quickly and forms larger inclusions which are readily eliminated, provided the slag is not too thick. It has been found advisable to use some ferromanganese about 10 minutes before tapping to clean up any residual silica or other oxides which are present at this time.

5. Holding the steel in the ladle as long as possible is of direct benefit in eliminating nonmetallic matter. Holding the ladle of course has other advantages, in that it is better to pour the steel "on the cold side" rather than exceedingly hot.

Acknowledgment

Acknowledgments are made to the various departments of The Heppenstall Co. concerned with this investigation. Chemical analyses of the slags and iron oxide in the metal were determined by J. F. Sanderson, S. S. Johnston, and W. C. Miller of the United States Bureau of Mines laboratory staff.

SOME PHYSICAL PROPERTIES OF HIGH SPEED STEEL

By Joseph V. Emmons

Abstract

A study is made of a high speed steel of the familiar 18-4-1 type. Hardening and drawing temperatures are varied through wide ranges and the effect of the variations on some of the physical properties of the steel is examined.

The mechanical properties of strength and plasticity are measured by a torsion method. A numerical value for toughness is calculated. The Rockwell hardness is determined and a study is made of the microstructure at a high magnification. Typical photomicrographs are shown illustrating some of the most interesting structures. Stress-strain curves are plotted and a graphic analysis made of the response of the properties to heat treatment. The results for the different properties are correlated and conclusions are drawn as to the causes of some of the variations observed.

THE properties of high speed steel have in the past been enumerated in terms more descriptive than exact. Such names as "cutting quality" and "red hardness," have been favorites but exact methods of measurement of such vague properties have been difficult to work out. The need for more fundamental data on the effect of heat treatment on the mechanical properties and the lack of understanding of the relation of the properties to each other has been long felt.

Soon after the development of the methods of measuring the physical properties of strength, plasticity and toughness by means of the torsion test as previously described[1], it was determined to investigate the effect of different variations of heat treatment on these properties of high speed steel.

Consideration of the investigations previously made on measurable properties of high speed steel revealed the following situation:

[1] J. V. Emmons, "Some Physical Properties of Hardened Tool Steel," *Proceedings*, American Society for Testing Materials, Vol. 31, 1931.

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, Joseph V. Emmons, is a member of the society. He is metallurgist for the Cleveland Twist Drill Co., Cleveland. Manuscript received June 20, 1931.

Hardness has been the property most widely studied. The work of Grossmann and Bain[2] gives an excellent picture of the response of the Rockwell hardness to various hardening and drawing treatments.

The property of strength has had less attention. Barry[3, 4] has investigated the flexural strength of small wires, while d'Arcambal[5] and Page[6] have made observations by the tensile method. The property of plasticity has received no serious attention while the property of toughness has been investigated by means of impact methods by Barry[4], and by means of bending methods by Barry[3] and Heller[7].

It was planned in this research to determine the response of the mechanical properties of strength, plasticity, toughness and hardness, to a wide range of variations in heat treatment. The investigation was confined to a single typical analysis of high speed steel of the most common type. The composition of this steel was as follows:

	Per Cent		Per Cent
Carbon	0.69	Sulphur	0.021
Manganese	0.17	Chromium	3.72
Phosphorus	0.019	Tungsten	18.17
Silicon	0.30	Vanadium	1.00

The raw material was in the form of a coil of wire rod. This coil was carefully inspected on both ends to insure that it was free from segregation or other defects. It was then cold drawn to the $\frac{5}{16}$ inch size required for the test specimens. The microstructure of the annealed steel after drawing is shown in Fig. 1. Great care was exercised that all of the test specimens were machined in an identical manner.

The variations in heat treatment were confined to hardening and drawing temperatures. All other possible variables such as soaking times and quenching speeds were held constant. No preheating was

[2]M. A. Grossmann and E. C. Bain, "High Speed Steel," (1931), John Wiley and Sons, p. 137.

[3]R. K. Barry, "Hardness and Toughness of High Speed Steel as Affected by Heat Treatment," TRANSACTIONS, American Society for Steel Treating, Vol. 10, 1926, p. 257.

[4]R. K. Barry, "Comparisons of Impact and Slow Bend Tests of High Speed Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 630.

[5]A. H. d'Arcambal, "Physical Tests on High Speed Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 2, 1922, p. 586.

[6]A. R. Page, "Mechanical Properties of High Speed Steel at Elevated Temperatures," *Metallurgia* (London) Vol. 1, 1930, p. 239.

[7]Alfred Heller, "Selection and Hardening of High Speed Steels," *American Machinist*, Vol. 74, 1931, Nos. 17, 18, 19.

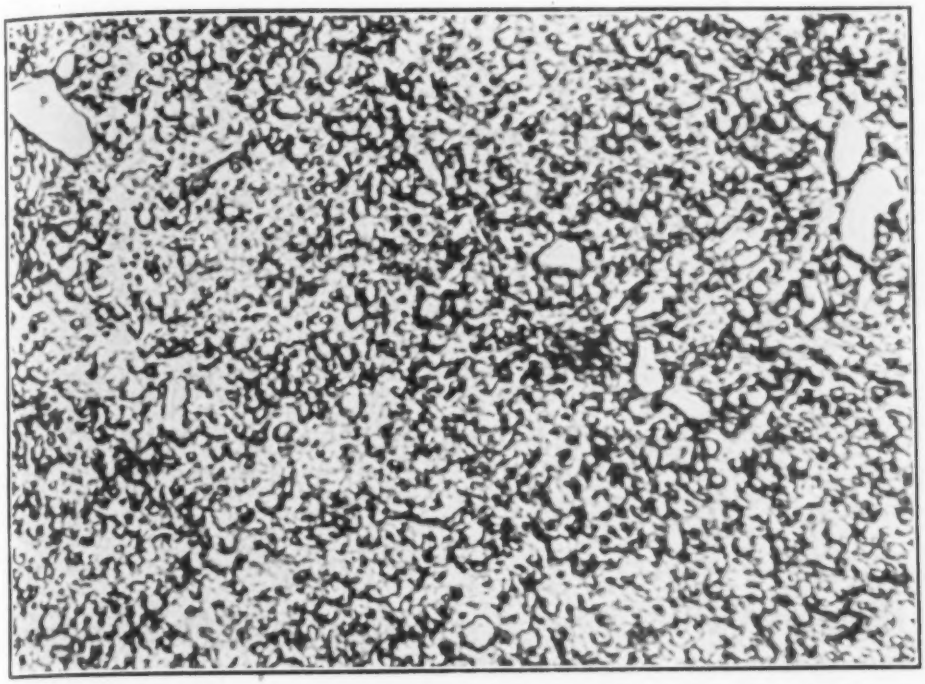

Fig. 1—High Speed Steel, Annealed Structure, Before Hardening, × 2000.

used. The hardening was done in a salt bath. The soaking time after the specimens had arrived at the hardening temperature was 30 seconds. The quench was in oil at about 100 degrees Fahr. The higher draws were performed in a lead bath, while the lower ones were in an oil bath. The drawing time was 30 minutes after the specimens arrived at the drawing temperature. The cooling from the draw was in still air. Every precaution was taken to keep the specimens straight during the heat treatment and no straightening was done before testing. In order to secure a good average of the results, three specimens were used for each heat treatment requiring 195 in all. Specimens were hardened at the following temperatures: 2200, 2250, 2300, 2350, 2400 degrees Fahr. (1204, 1231, 1259, 1286, 1315 degrees Cent.). Three specimens from each hardening temperature were drawn as follows: No draw, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300 degrees Fahr. (93, 149, 204, 260, 315, 371, 426, 482, 538, 593, 648, 704 degrees Cent.).

The specimens were then broken in torsion, the angular deformation being recorded at increments in torque of approximately 25 inch-pounds. It is not possible to show the detailed observations of all of the specimens in the limited space of this paper but a typical record

Table I

Record Sheet of Torsion Test, Observations on the Three Specimens Hardened at 2350 degrees Fahr. (1285 degrees Cent.) and Drawn at 1000 degrees Fahr. (540 degrees Cent.)

Torque in Pounds at 1 inch Radius	Angular Deformation in Degrees of Circular Measure			
Specimen No.	145	146	147	Average
25	4	4	4	4
50	7	8	8	8
75	11	11	11	11
100	15	15	15	15
126	18	18	18	18
154	22	23	22	22
180	26	27	26	26
205	31	31	30	31
232	35	36	36	36
260	42	43	42	42
287	48	49	48	48
315	56	56	54	55
341	63	63	63	63
367	74	75	74	74
394	88	89	86	88
423	108	116	111	112
452	150	157	153	153
Ultimate Angle, Degrees	187	196	247	210
Ultimate Torque, Inches-Pounds.	467	467	473	469

of the observations on the specimens hardened at 2350 degrees Fahr. (1285 degrees Cent.) and drawn at 1000 degrees Fahr. (540 degrees Cent.), is shown in Table I. The observations of the ultimate torque are shown in Table II, while those of the ultimate deformation are shown in Table III, the three specimens at each heat treatment being averaged together. As it was desired to distinguish between the elastic and the plastic deformation, a graphic calculation to this end was made in the following manner: A typical stress-strain curve was plotted from the observations shown in Table I. This curve is shown in Fig. 2. The straight portion of the curve was then extended as a broken line to the top of the chart and was taken as representing the elastic deformation. As the slope of the line of proportionality does not appear to be affected by the variations in heat treatment, it represents the elastic deformation of any of the specimens at any load. The ultimate deformation minus the elastic deformation at the ultimate load is the ultimate plastic deformation. In Fig. 2, the distance AC is the total deformation, AB is the elastic deformation, and BC is the plastic deformation. The calculated plastic deformation results are recorded as shown in Table IV, the values given being the average of the three specimens at each heat treatment.

In order to obtain a numerical value for toughness, it was assumed that a very tough steel would owe its toughness equally to the two properties, strength and ability to withstand deformation. For

Table II

Observations of The Ultimate Torque in Inch-Pounds

Heat Treatment							
Hardening Temperatures		Drawing Temperatures		Specimens			Average
Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.				
2200	1205	No Draw		367	378	315	353
		200	95	384	384	325	364
		300	150	362	411	367	380
		400	205	423	417	417	419
		500	260	394	394	400	396
		600	315	394	389	389	391
		700	370	394	389	389	391
		800	425	389	389	378	385
		900	480	400	394	400	398
		1000	540	406	411	411	409
		1100	595	373	378	373	375
		1200	660	315	315	310	313
		1300	705	210	210	210	210
2250	1230	No Draw		330	367	357	351
		200	95	341	315	352	336
		300	150	341	357	384	361
		400	205	435	417	435	429
		500	260	406	406	406	406
		600	315	406	394	394	398
		700	370	406	400	389	398
		800	425	400	400	406	402
		900	480	417	411	417	415
		1000	540	423	429	429	427
		1100	595	389	400	394	394
		1200	650	330	330	325	328
		1300	705	215	215	215	215
2300	1260	No Draw		357	341	341	346
		200	95	362		362	362
		300	150	400	362	389	384
		400	205	441	441	446	443
		500	260	429	423	429	427
		600	315	417	411	417	415
		700	370	417	417	423	419
		800	425	423	429	423	425
		900	480	435	423	417	425
		1000	540	457	441	452	450
		1100	595	417	417	411	415
		1200	650	341	336	341	339
		1300	705	226	226	226	226
2350	1285	No Draw		287	282	276	282
		200	95	287	287	276	283
		300	150	298	287	298	294
		400	205	389	406	423	406
		500	260	423	429	429	427
		600	315	394	417	406	406
		700	370	417	417	417	417
		800	426	423	423	417	421
		900	480	441	429	441	437
		1000	540	467	467	473	469
		1100	595	423	417	429	423
		1200	650	357	362	357	359
		1300	705	232	232	232	232
2400	1315	No Draw		232	232	215	226
		200	95	220	220	232	226
		300	150	271	232	254	252
		400	205	394	367	367	376
		500	260	389	389	384	387
		600	315	394	394	384	391
		700	370	389	389	389	389
		800	425	394	378	417	396
		900	480	394	400	400	398
		1000	540	417	406	423	415
		1100	595	446	435	441	441
		1200	650	373	384	389	382
		1300	705	243	243	238	241

Table III

Observations of The Ultimate Angular Deformation in Degrees of Circular Measure

Heat Treatment							
Hardening Temperatures		Drawing Temperatures					
Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.	Specimens			Average
2200	1205	No Draw		76	83	58	72
		200	95	84	84	61	76
		300	150	71	114	77	87
		400	205	240	203	214	219
		500	260	204	208	212	208
		600	315	240	226	222	229
		700	370	260	254	255	256
		800	425	276	287	178	247
		900	480	324	322	320	322
		1000	540	190	258	258	235
		1100	595	220	208	188	205
		1200	650	286	172	176	211
		1300	705	334	306	346	329
2250	1230	No Draw		66	72	77	72
		200	95	64	56	71	64
		300	150	62	68	87	72
		400	205	244	159	256	220
		500	260	184	176	174	178
		600	315	245	165	154	188
		700	370	308	240	166	238
		800	425	243	224	284	250
		900	480	352	336	314	334
		1000	540	238	242	250	243
		1100	595	130	228	174	177
		1200	650	222	238	266	242
		1300	705	296	334	306	312
2300	1260	No Draw		80	72	71	74
		200	95	80		81	81
		300	150	93	73	86	84
		400	205	248	195	276	240
		500	260	304	255	245	268
		600	315	252	244	230	242
		700	370	292	270	298	287
		800	425	290	304	298	297
		900	480	325	280	192	266
		1000	540	252	194	248	231
		1100	595	181	203	190	191
		1200	650	263	198	250	237
		1300	705	335	360	312	336
2350	1285	No Draw		58	58	57	58
		200	95	54	54	54	54
		300	150	54	48	55	52
		400	205	110	128	188	142
		500	260	252	285	282	273
		600	315	142	256	197	198
		700	370	237	278	270	262
		800	425	316	306	270	297
		900	480	314	272	320	302
		1000	540	187	196	247	210
		1100	595	120	105	142	122
		1200	650	172	154	199	175
		1300	705	322	318	348	329
2400	1315	No Draw		50	49	45	48
		200	95	44	45	47	45
		300	150	53	40	47	47
		400	205	145	104	112	120
		500	260	161	174	160	165
		600	315	210	180	168	186
		700	370	186	172	192	183
		800	425	154	117	230	167
		900	480	126	148	135	136
		1000	540	110	103	119	111
		1100	595	123	120	118	120
		1200	650	121	148	136	133
		1300	705	272	297	242	270

Table IV

Summary of the Ultimate Torque and Ultimate Deformation Together with the Calculated Plastic Deformation

Heat Treatment							
Hardening Temperatures		Drawing Temperatures		Ultimate Torque	Ultimate Deformation	Elastic Deformation	Plastic Deformation
Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.				
2200	1205	No Draw		353	72	49	23
		200	95	364	76	50	26
		300	150	380	87	53	34
		400	205	419	219	58	161
		500	260	396	208	55	153
		600	315	391	229	54	175
		700	370	391	256	54	202
		800	425	385	247	54	193
		900	480	398	322	55	267
		1000	540	409	235	57	178
		1100	595	375	205	52	153
		1200	650	313	211	44	167
		1300	705	210	329	30	299
2250	1230	No Draw		351	72	49	23
		200	95	336	64	47	17
		300	150	361	72	50	22
		400	205	429	220	59	161
		500	260	406	178	56	122
		600	315	398	188	55	133
		700	370	398	238	55	183
		800	425	402	250	56	194
		900	480	415	334	58	276
		1000	540	427	243	59	184
		1100	595	394	177	55	122
		1200	650	328	242	46	196
		1300	705	215	312	30	282
2300	1260	No Draw		346	74	48	26
		200	95	362	81	50	31
		300	150	384	84	54	30
		400	205	443	240	61	179
		500	260	427	268	59	209
		600	315	415	242	58	184
		700	370	419	287	58	229
		800	425	425	297	59	238
		900	480	425	266	59	207
		1000	540	450	231	62	169
		1100	595	415	191	58	133
		1200	650	339	237	47	190
		1300	705	226	336	32	304
2350	1285	No Draw		282	58	40	18
		200	95	283	54	40	14
		300	150	294	52	41	11
		400	205	406	142	56	86
		500	260	427	273	59	214
		600	315	406	198	56	142
		700	370	417	262	58	204
		800	425	421	297	58	239
		900	480	437	302	60	242
		1000	540	469	210	65	145
		1100	595	423	122	59	63
		1200	650	359	175	50	125
		1300	705	232	329	33	296
2400	1315	No Draw		226	48	32	16
		200	95	226	45	32	13
		300	150	252	47	35	12
		400	205	376	120	52	68
		500	260	387	165	54	111
		600	315	391	186	54	132
		700	370	389	183	54	129
		800	425	396	167	55	112
		900	480	398	136	55	81
		1000	540	415	111	58	53
		1100	595	441	120	61	59
		1200	650	382	133	53	80
		1300	705	241	270	34	236

this particular specimen and method the ultimate torque in inch-pounds is representative of the strength and the ultimate deformation in degrees of twist indicates the ability to withstand deformation. It has been found that in steels of great toughness, these numerical values are about equal. A product of these two values combines strength and deformation in about equal proportions and has been called a coefficient of toughness. It is regarded as a rough, but some-

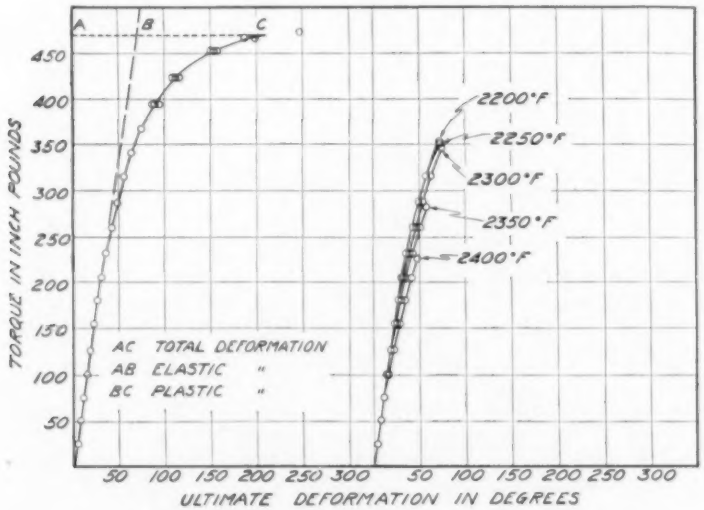

Fig. 2—Typical Stress-Strain Curve for Calculation of the Plastic Deformation.
Fig. 3—Stress-Strain Curves with no Draw.

times a useful indication of the toughness of hardened steels. In Table V are recorded the calculations of the coefficient of toughness for the various specimens. In each case the values for the three specimens at each heat treatment are averaged together. The values are only regarded as significant to the nearest thousand.

For purpose of comparison the hardness was determined upon all specimens using the Rockwell method with the "C" Scale. The hardness tests were made after the completion of the torsion tests. The determinations were upon a flat of the short end of the torsion specimen. Five determinations were made upon each specimen, making fifteen results for each variation of heat treatment. These results are averaged and summarized in Table VI.

Microscopic examination was made of specimens at all heat treatment in order to determine the effect on the structure of the several variations for purpose of comparison with the physical properties. A magnification of 2000 diameters was found to be the most

suitable for the purpose of record and typical photomicrographs were taken.

Analysis of the Results

Stress-Strain Curves: Stress-strain curves were first plotted from the average results of the set of specimens representing each heat treatment. These are shown in Figs. 3 to 15. For the purpose

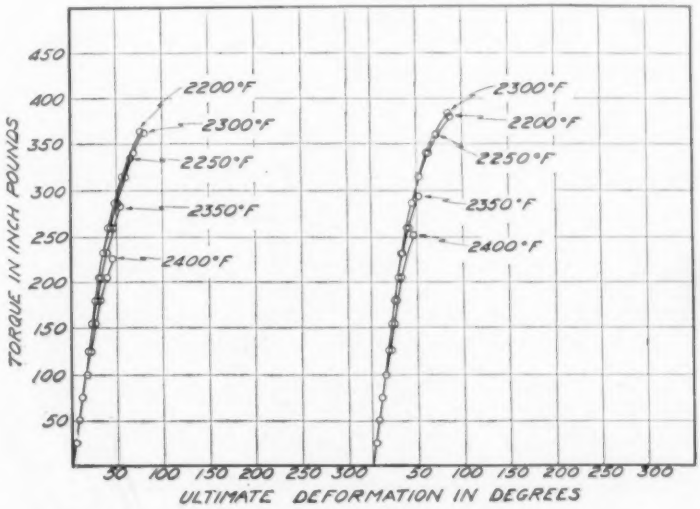

Fig. 4—Stress-Strain Curves at the 200 Degrees Fahr. (95 Degrees Cent.) Draw.

Fig. 5—Stress-Strain Curves at the 300 Degrees Fahr. (150 Degrees Cent.) Draw.

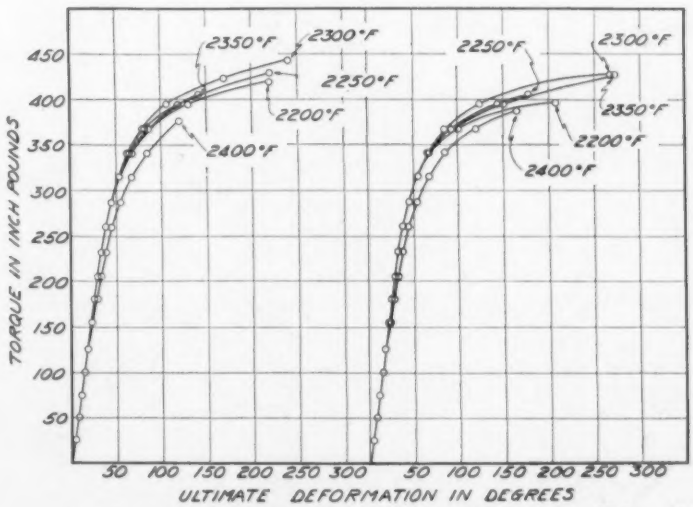

Fig. 6—Stress-Strain Curves at the 400 Degrees Fahr. (205 Degrees Cent.) Draw.

Fig. 7—Stress-Strain Curves at the 500 Degrees Fahr. (260 Degrees Cent.) Draw.

of ready comparison, the curves for the five hardening temperatures at each draw are plotted in one figure. Stress-strain curves are particularly useful in a study of the properties of metals, because of the

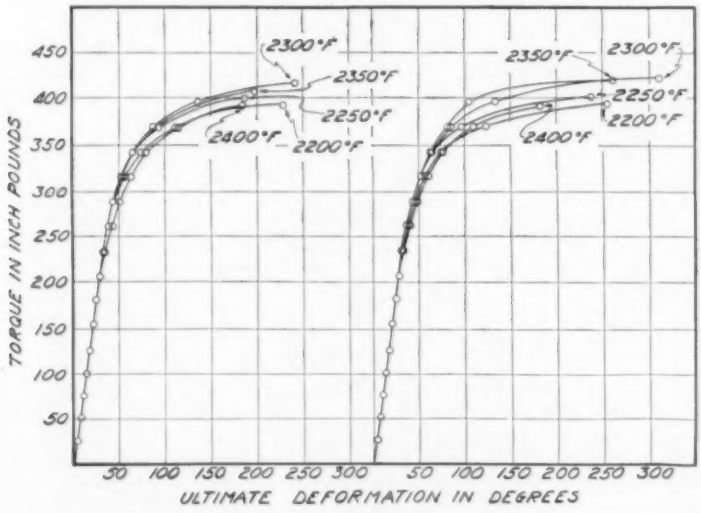

Fig. 8—Stress-Strain Curves at the 600 Degrees Fahr. (315 Degrees Cent.) Draw.
Fig. 9—Stress-Strain Curves at the 700 Degrees Fahr. (370 Degrees Cent.) Draw.

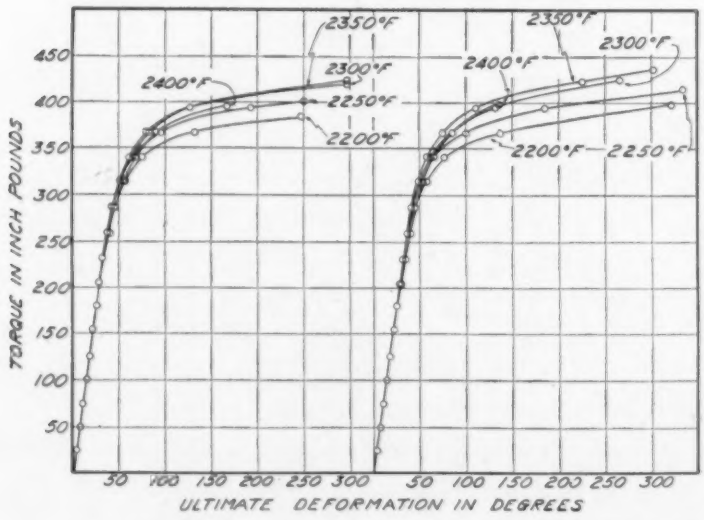

Fig. 10—Stress-Strain Curves at the 800 Degrees Fahr. (425 Degrees Cent.) Draw.
Fig. 11—Stress-Strain Curves at the 900 Degrees Fahr. (480 Degrees Cent.) Draw.

general picture which they give of several mechanical properties. It is first observed that while both the hardening and the drawing temperatures have an effect upon the shape of the curves, that of the

Table V

Calculated Coefficients of Toughness

Heat Treatment						
Hardening Temperatures		Drawing Temperatures		Ultimate Torque	Ultimate Deformation	Product = Coefficient of
Deg. Fahr.	Deg. Cent.	Deg. Fahr.	Deg. Cent.	Inch-Pounds	Degrees	Toughness
2200	1205	No Draw		353	72	25,000
		200	95	364	76	28,000
		300	150	380	87	33,000
		400	205	419	219	92,000
		500	260	396	208	82,000
		600	315	391	229	90,000
		700	370	391	256	100,000
		800	425	385	247	95,000
		900	480	398	322	128,000
		1000	540	409	235	96,000
		1100	595	375	205	77,000
		1200	650	313	211	66,000
		1300	705	210	329	69,000
2250	1230	No Draw		351	72	25,000
		200	95	336	64	22,000
		300	150	361	72	26,000
		400	205	429	220	94,000
		500	260	406	178	72,000
		600	315	398	188	75,000
		700	370	398	238	95,000
		800	425	402	250	100,000
		900	480	415	334	139,000
		1000	540	427	243	104,000
		1100	595	394	177	70,000
		1200	650	328	242	76,000
		1300	705	215	312	67,000
2300	1260	No Draw		346	74	26,000
		200	95	362	81	29,000
		300	150	384	84	32,000
		400	205	443	240	106,000
		500	260	427	268	114,000
		600	315	415	242	100,000
		700	370	419	287	120,000
		800	425	425	297	126,000
		900	480	425	266	113,000
		1000	540	450	231	104,000
		1100	595	415	191	79,000
		1200	650	339	237	80,000
		1300	705	226	336	76,000
2350	1285	No Draw		282	58	16,000
		200	95	283	54	15,000
		300	150	294	52	15,000
		400	205	406	142	58,000
		500	260	427	273	117,000
		600	315	406	198	80,000
		700	370	417	262	109,000
		800	425	421	297	125,000
		900	480	437	302	132,000
		1000	540	469	210	99,000
		1100	595	423	122	52,000
		1200	650	359	175	63,000
		1300	705	232	329	76,000
2400	1315	No Draw		226	48	11,000
		200	95	226	45	10,000
		300	150	252	47	12,000
		400	205	376	120	45,000
		500	260	387	165	64,000
		600	315	391	186	73,000
		700	370	389	183	71,000
		800	425	396	167	66,000
		900	480	398	136	54,000
		1000	540	415	111	46,000
		1100	595	441	120	53,000
		1200	650	382	133	51,000
		1300	705	241	270	65,000

Table VI

Rockwell Hardness Determinations on the C Scale

Heat Treatment: Hardening Temperatures Deg. Fahr.	Hardening Temperatures Deg. Cent.	Drawing Temperatures Deg. Fahr.	Drawing Temperatures Deg. Cent.	Averages of 5 Determinations on Each Specimen			General Average
2200	1205	No Draw		65.2	65.2	65.7	65.4
		200	95	65.3	65.2	65.3	65.3
		300	150	62.7	64.2	62.7	63.2
		400	205	61.9	61.8	61.7	61.8
		500	260	60.5	61.1	60.3	60.6
		600	315	60.0	60.4	60.5	60.3
		700	370	59.7	60.6	60.3	60.2
		800	425	59.9	60.0	60.0	60.0
		900	480	60.5	60.7	60.6	60.6
		1000	540	61.3	61.3	61.4	61.3
		1100	595	59.2	59.7	59.2	59.4
		1200	650	54.6	55.1	54.2	54.6
		1300	705	46.3	44.1	44.6	45.0
2250	1230	No Draw		64.1	63.5	63.9	63.8
		200	95	63.9	64.0	64.1	64.0
		300	150	63.9	63.7	63.7	63.8
		400	205	62.9	62.6	62.3	62.6
		500	260	61.7	61.9	61.9	61.8
		600	315	61.5	61.5	61.1	61.4
		700	370	61.3	61.2	61.2	61.2
		800	425	61.3	61.4	61.1	61.3
		900	480	61.8	61.9	61.8	61.8
		1000	540	62.9	63.1	62.9	63.0
		1100	595	60.6	60.9	60.8	60.8
		1200	650	55.2	55.7	55.3	55.4
		1300	705	45.7	45.5	45.0	45.4
2300	1260	No Draw		64.3	66.1	64.6	65.0
		200	95	65.2	63.5	64.2	64.3
		300	150	62.9	63.1	64.5	63.5
		400	205	63.3	63.0	62.7	63.0
		500	260	62.3	62.5	62.5	62.4
		600	315	62.5	62.1	62.3	62.3
		700	370	62.3	62.5	62.5	62.4
		800	425	62.7	62.1	62.7	62.5
		900	480	63.1	63.3	63.3	63.3
		1000	540	64.4	64.1	64.3	64.3
		1100	595	62.0	62.1	62.7	62.3
		1200	650	56.8	56.4	56.8	56.7
		1300	705	46.2	46.2	46.7	46.4
2350	1285	No Draw		65.3	64.1	65.4	64.9
		200	95	65.7	65.9	65.9	65.8
		300	150	65.1	65.3	64.0	64.8
		400	205	63.4	63.7	63.1	63.4
		500	260	61.7	62.0	62.1	61.9
		600	315	61.7	61.9	61.6	61.7
		700	370	62.0	62.1	62.0	62.0
		800	425	62.2	62.5	62.1	62.3
		900	480	63.5	63.2	63.0	63.2
		1000	540	64.6	64.7	64.7	64.7
		1100	595	63.4	63.1	63.5	63.3
		1200	650	58.0	58.1	58.0	58.0
		1300	705	47.0	46.3	48.1	47.1
2400	1315	No Draw		65.1	65.5	65.2	65.3
		200	95	65.2	65.2	65.7	65.4
		300	150	65.2	65.0	65.0	65.1
		400	205	63.5	63.1	63.0	63.2
		500	260	61.6	61.9	61.7	61.7
		600	315	61.0	60.8	61.2	61.0
		700	370	60.9	60.9	61.7	61.2
		800	425	62.5	62.2	63.0	62.6
		900	480	63.4	63.3	63.2	63.3
		1000	540	64.9	65.5	65.7	65.4
		1100	595	64.7	64.7	64.6	64.7
		1200	650	59.8	59.9	59.4	59.7
		1300	705	48.1	48.4	48.8	48.4

drawing temperatures is more pronounced than hardening temperatures.

The hardening temperatures at no draw produce an effect upon the general plasticity in that the plastic deformation increases with

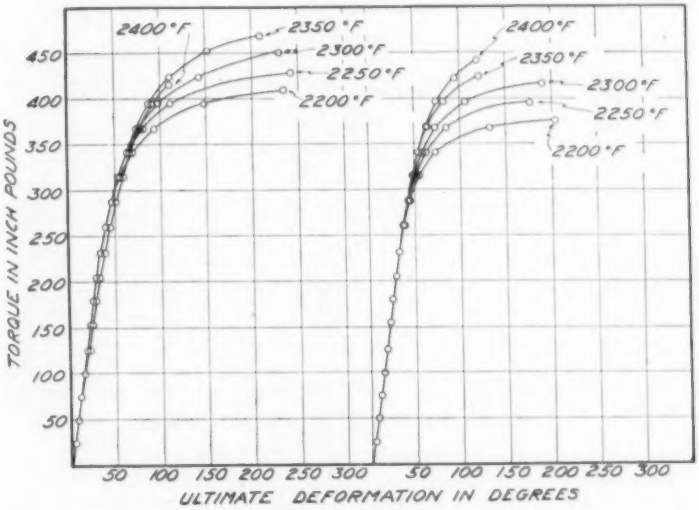

Fig. 12—Stress-Strain Curves at the 1000 Degrees Fahr. (540 Degrees Cent.) Draw.
Fig. 13—Stress-Strain Curves at the 1100 Degrees Fahr. (595 Degrees Cent.) Draw.

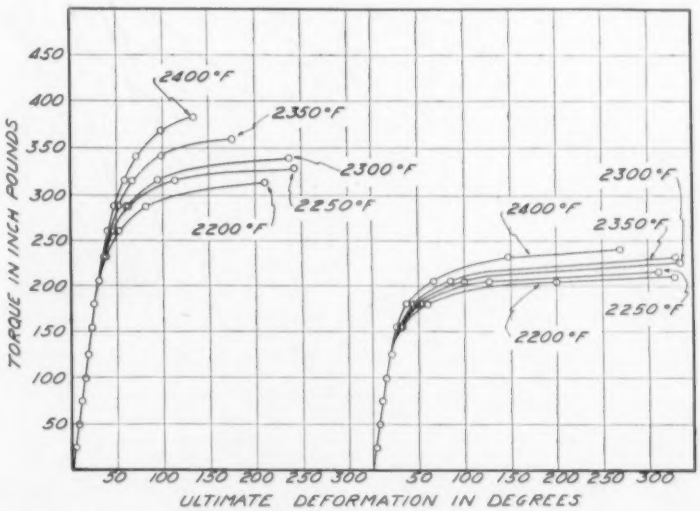

Fig. 14—Stress-Strain Curves at the 1200 Degrees Fahr. (650 Degrees Cent.) Draw.
Fig. 15—Stress-Strain Curves at the 1300 Degrees Fahr. (705 Degrees Cent.) Draw.

increasing hardening temperatures. See Fig. 3. This change is within narrow limits. In the same figure the strength decreases with increasing hardening temperatures. Drawing brings about a gradual

reversal of this order until at draws 1100 degrees Fahr. (595 degrees Cent.) and higher, increasing hardening temperatures decrease the plasticity and increase the strength. See Figs. 13, 14, 15.

There are three regions of drawing temperatures in which the stress-strain curves vary so definitely that profound changes in the

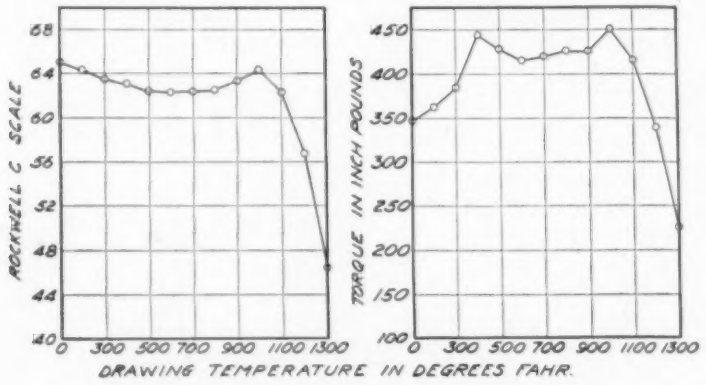

Fig. 16—Rockwell Hardness Versus Drawing Temperatures, Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.).
Fig. 17—Ultimate Torque Versus Drawing Temperatures, Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.).

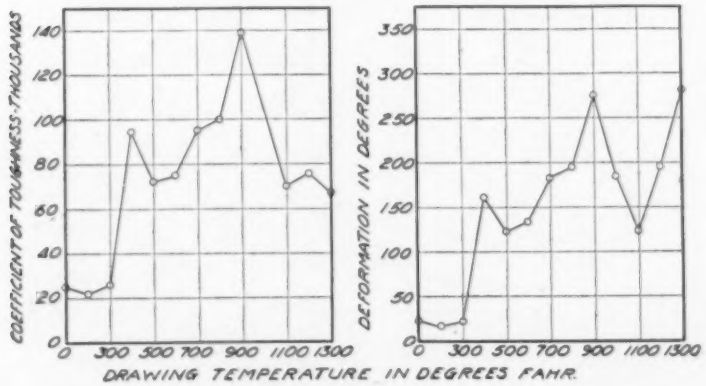

Fig. 18—Coefficient of Toughness Versus Drawing Temperatures, Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.).
Fig. 19—Plastic Deformation Versus Drawing Temperatures, Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.).

character of the steel are indicated. The first and most pronounced of these variations is observed between draw 300 degrees Fahr., Fig. 5, and draw 400 degrees Fahr., Fig. 6, where there is a sudden increase in both the strength and the plasticity. The second variation is between 900 degrees Fahr. (480 degrees Cent.) and 1000 degrees Fahr. (540 degrees Cent.), where the strength again increases while the plasticity decreases. The third variation is between 1100 degrees

Fahr. (595 degrees Cent.), and 1200 degrees Fahr. (650 degrees Cent.), where the strength decreases and the plasticity begins to increase again.

Rockwell Hardness

The response of the Rockwell hardness to variations in heat treatment is shown by two sets of curves. The hardness is plotted

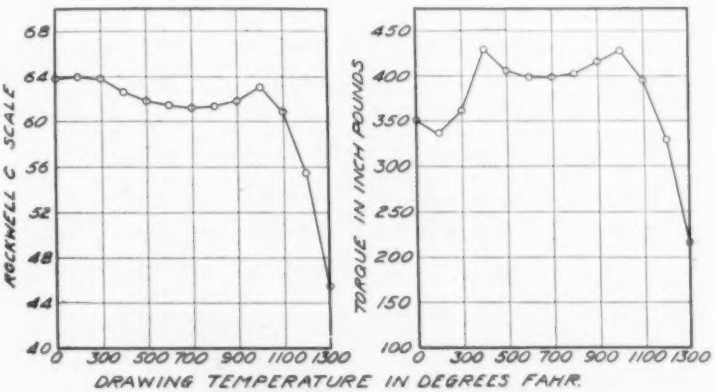

Fig. 20—Rockwell Hardness Versus Drawing Temperatures, Hardened at 2250 Degrees Fahr. (1230 Degrees Cent.).
Fig. 21—Ultimate Torque Versus Drawing Temperatures, Hardened at 2250 Degrees Fahr. (1230 Degrees Cent.).

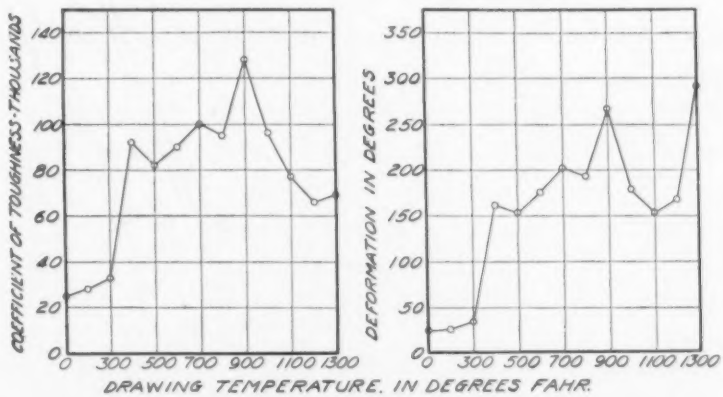

Fig. 22—Coefficient of Toughness Versus Drawing Temperatures, Hardened at 2250 Degrees Fahr. (1230 Degrees Cent.).
Fig. 23—Plastic Deformation Versus Drawing Temperatures, Hardened at 2250 Degrees Fahr. (1230 Degrees Cent.).

against drawing temperatures in Figs. 16, 20, 24, 28, 32, while in Fig. 36 it is plotted against hardening temperatures. The general shape of the curves of hardness versus drawing temperatures is familiar, having been shown previously by many investigators. The curves here presented are particularly interesting because of the complete

range of drawing temperatures covered and because of the changes produced by hardening at different temperatures. But little difference in the hardness is observed for the several hardening temperatures unless the specimens are drawn to 300 degrees Fahr. (150 degrees Cent.) or higher. From draws of 400 degrees Fahr. to 800 degrees Fahr. (200-425 degrees Cent.), the highest hardness is produced by the hardening temperature of 2300 degrees Fahr. (1260 degrees Cent.). From 1000 degrees Fahr. to 1300 degrees Fahr. (540-705 degrees Cent.), the highest hardness is at the hardening temperature of 2400 degrees Fahr. (1315 degrees Cent.). The peak of secondary hardness occurs at 1000 degrees Fahr. (540 degrees Cent.), although it appears probable that closer spaced drawing temperatures would have shown the actual peak to be somewhat higher. The highest observed hardness was at the hardening temperature of 2350 degrees Fahr. (1285 degrees Cent.), with a draw of 200 degrees Fahr. (95 degrees Cent.), where a value of C 65.8 was recorded.

Ultimate Torsional Strength

The term ultimate torque, as used in this experiment, is the total load in inch pounds, at the breaking point. The ultimate torsional strength in the outermost fibers is not used because means of calculating its value are open to question in the case of varying plasticity such as we have here. The highest observed torque in the experiment was in the specimens hardened at 2350 degrees Fahr. (1285 degrees Cent.), and drawn at 1000 degrees Fahr. (540 degrees Cent.). The ultimate torsional strength in the outermost fibers for these specimens was calculated to be 363,000 pounds per square inch.

Ultimate Torque

The ultimate torque is a function of the strength and the more familiar term strength is often used in the text, meaning the ultimate torque. Curves showing the ultimate torque plotted against drawing temperatures are shown in Figs. 17, 21, 25, 29, 33. In Fig. 37, the ultimate torque is plotted against varying hardening temperatures. Both hardening and drawing variations have a definite effect upon the strength. The curves in Figs. 17, 21, 25, 29, 33, show a double peak, which is quite interesting. The first peak occurs at drawing temperatures about 400 degrees Fahr. (205 degrees Cent.), and is more important at the lower hardening temperatures, while at a hardening

temperature of 2400 degrees Fahr. (1315 degrees Cent.), it almost disappears. These two peaks of strength roughly mark the two ranges of drawing temperatures most commonly used for high speed tools. The curves in Fig. 37 show some remarkable variations in shape for the different drawing temperatures. For the specimens not drawn, the highest strength is at 2200 degrees Fahr. (1205 degrees

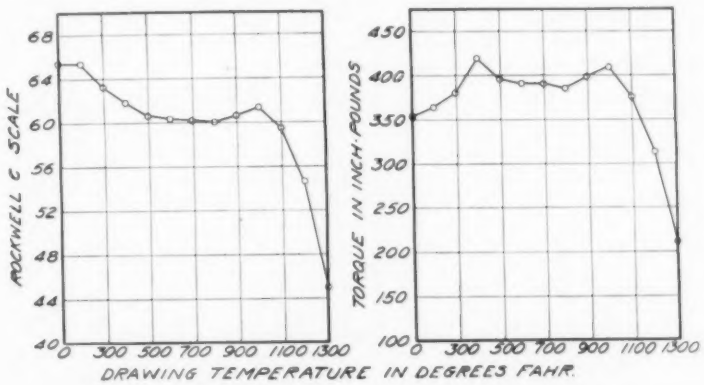

Fig. 24—Rockwell Hardness Versus Drawing Temperatures, Hardened at 2300 Degrees Fahr. (1260 Degrees Cent.).
Fig. 25—Ultimate Torque Versus Drawing Temperatures, Hardened at 2300 Degrees Fahr. (1260 Degrees Cent.).

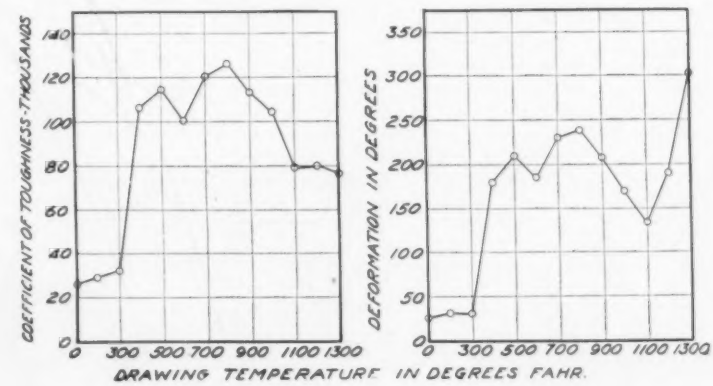

Fig. 26—Coefficient of Toughness Versus Drawing Temperatures, Hardened at 2300 Degrees Fahr. (1260 Degrees Cent.).
Fig. 27—Plastic Deformation Versus Drawing Temperatures, Hardened at 2300 Degrees Fahr. (1260 Degrees Cent.).

Cent.), and the lowest strength at 2400 degrees Fahr. (1315 degrees Cent.). At the lower draws a peak of strength develops at 2300 degrees Fahr. (1260 degrees Cent.), at intermediate draws, the peak shifts to 2350 degrees Fahr. (1285 degrees Cent.), and at the higher draws it moves to 2400 degrees Fahr. (1315 degrees Cent.). The curves at 1100 degrees Fahr. (595 degrees Cent.), and higher are the reverse of those at no draw. It is obvious that these changing curves

are faithfully recording a complicated series of alterations in the constitution of the steel.

Plastic Deformation

The results for the plasticity have been particularly interesting because our previous knowledge of this property has been so vague. In Figs. 19, 23, 27, 31, 35, curves are plotted between plastic deform-

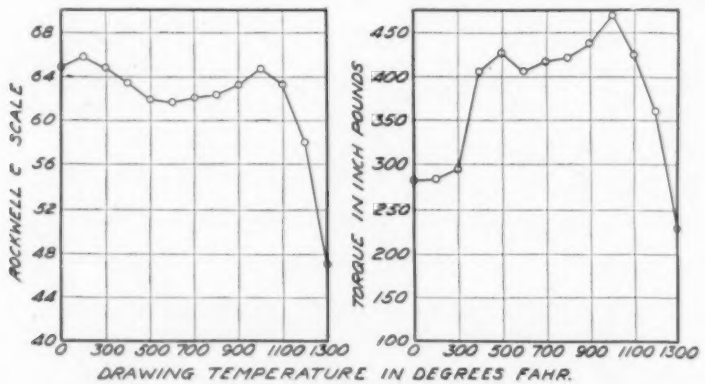

Fig. 28—Rockwell Hardness Versus Drawing Temperatures, Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.).
Fig. 29—Ultimate Torque Versus Drawing Temperatures, Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.).

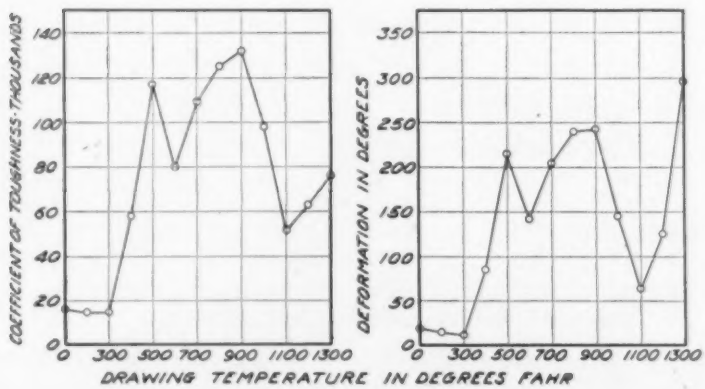

Fig. 30—Coefficient of Toughness Versus Drawing Temperatures, Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.).
Fig. 31—Plastic Deformation Versus Drawing Temperatures, Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.).

ation and drawing temperatures. These curves are complex and can be better visualized than described. In general, drawing temperatures below 400 degrees Fahr. (205 degrees Cent.) do not affect the plasticity. Higher drawing temperatures produce an increase in the plasticity which takes place in definite steps. At the hardening tem-

perature of 2200 degrees Fahr. (1205 degrees Cent.), there are four steps, at 2300 degrees Fahr. (1260 degrees Cent.), there are three steps and at 2400 degrees Fahr. (1315 degrees Cent.), there are but two. There is always a pronounced valley in the curve at the draw of 1100 degrees Fahr. (595 degrees Cent.). The hardening temperatures considered in Fig. 39 do not have as great an effect upon the

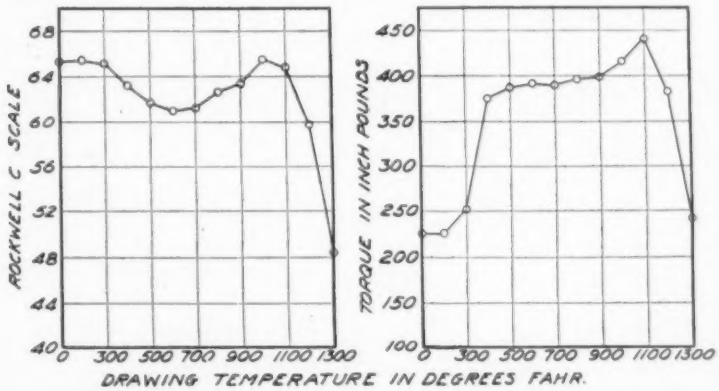

Fig. 32—Rockwell Hardness Versus Drawing Temperatures, Hardened at 2400 Degrees Fahr. (1315 Degrees Cent.).
Fig. 33—Ultimate Torque Versus Drawing Temperatures, Hardened at 2400 Degrees Fahr. (1315 Degrees Cent.).

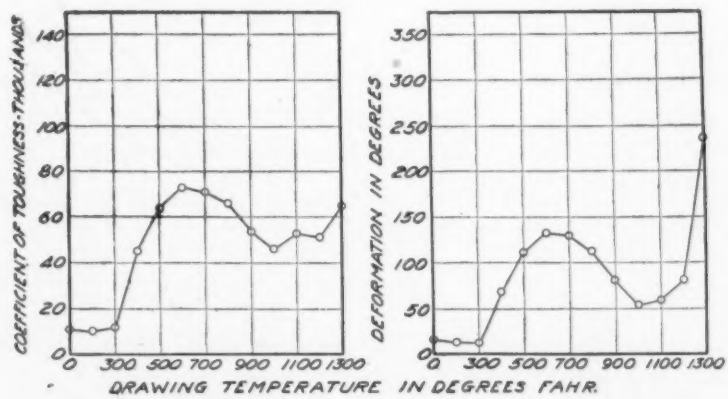

Fig. 34—Coefficient of Toughness Versus Drawing Temperatures, Hardened at 2400 Degrees Fahr. (1315 Degrees Cent.).
Fig. 35—Plastic Deformation Versus Drawing Temperatures, Hardened at 2400 Degrees Fahr. (1315 Degrees Cent.).

plasticity as the draws. 2400 degrees Fahr. (1315 degrees Cent.) always produces a low order of plasticity. There is generally a peak of plasticity at an intermediate hardening temperature such as 2300 degrees Fahr. (1260 degrees Cent.). The highest plasticity recorded was at 2300 degrees Fahr. (1260 degrees Cent.), with a draw of 1300 degrees Fahr. (705 degrees Cent.). A noteworthy observation

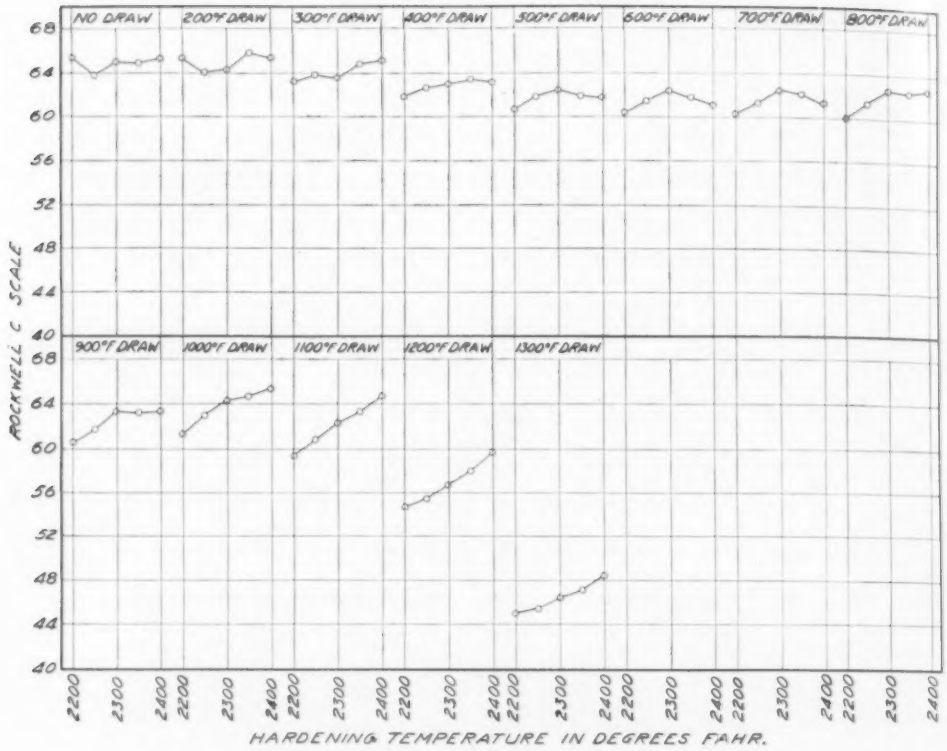

Fig. 36—Rockwell Hardness Versus Hardening Temperatures.

is the great peak of plasticity in the vicinity of the 900 degrees Fahr. (480 degrees Cent.) draw, which is not accompanied by any marked change in either hardness, strength or microstructure.

Coefficient of Toughness

The values obtained for the coefficient of toughness are regarded as being of practical utility rather than strictly scientific importance. Being an arbitrary combination of the properties of strength and plasticity, they indicate in a general way, the ability of the steel to withstand rough treatment and severe duty, without breakage. Curves showing the coefficients of toughness plotted against drawing temperatures are shown in Figs. 18, 22, 26, 30, 34. The most prominent feature of these curves is the outstanding peak in the general vicinity of the 900 degrees Fahr. (480 degrees Cent.), draw and the equally prominent valley which follows at the 1100 degrees Fahr. (595 degrees Cent.) draw. Drawing temperatures below 400 degrees Fahr. (205 degrees Cent.), have a low order of toughness. The hardening

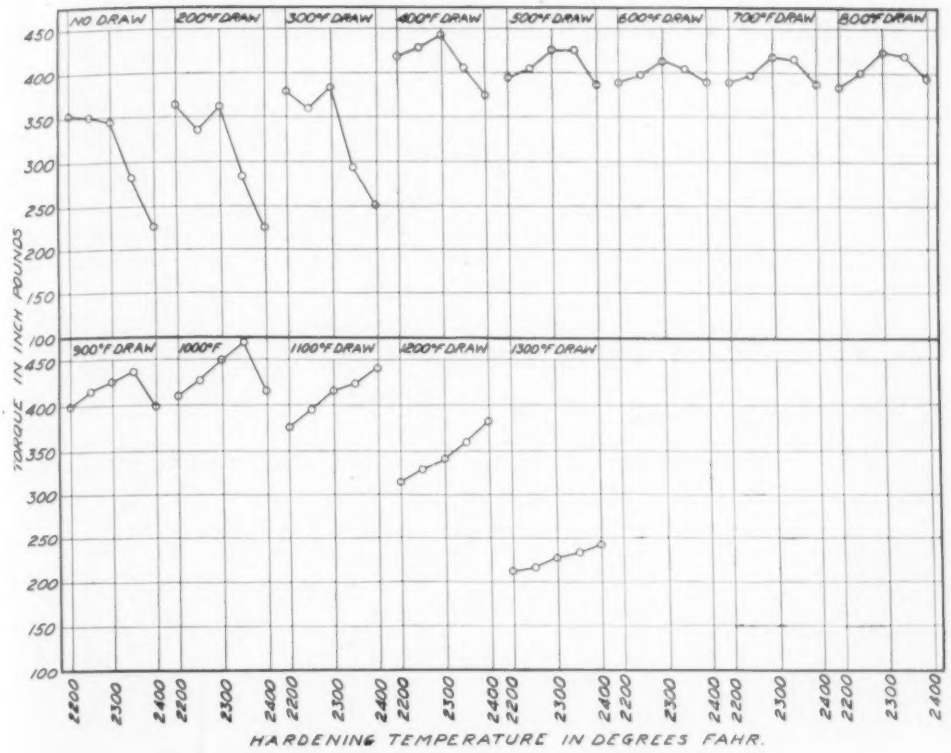

Fig. 37—Ultimate Torque Versus Hardening Temperatures.

temperatures shown in Fig. 38 have in all cases a peak of toughness at an intermediate temperature. Hardening at 2400 degrees Fahr. (1315 degrees Cent.) produces low toughness in every case. The highest peak of toughness is produced on the specimen hardened at 2250 degrees Fahr. (1230 degrees Cent.), and drawn at 900 degrees Fahr. (480 degrees Cent.).

Microstructure

The effect of varying hardening temperatures is shown in Figs. 40 to 44. It will be observed that increasing hardening temperatures produce the following effects:

First, increase in the grain size of the austenite; second, increase in the distinctness of the grain boundaries; third, decreased number of carbide masses; fourth, increase in the average size of the individual carbide masses. The effect of increasing drawing temperatures is shown in Figs. 45, 43, 46, 47, 48, in the order given. It is observed that the effect of the draw is primarily upon the structure

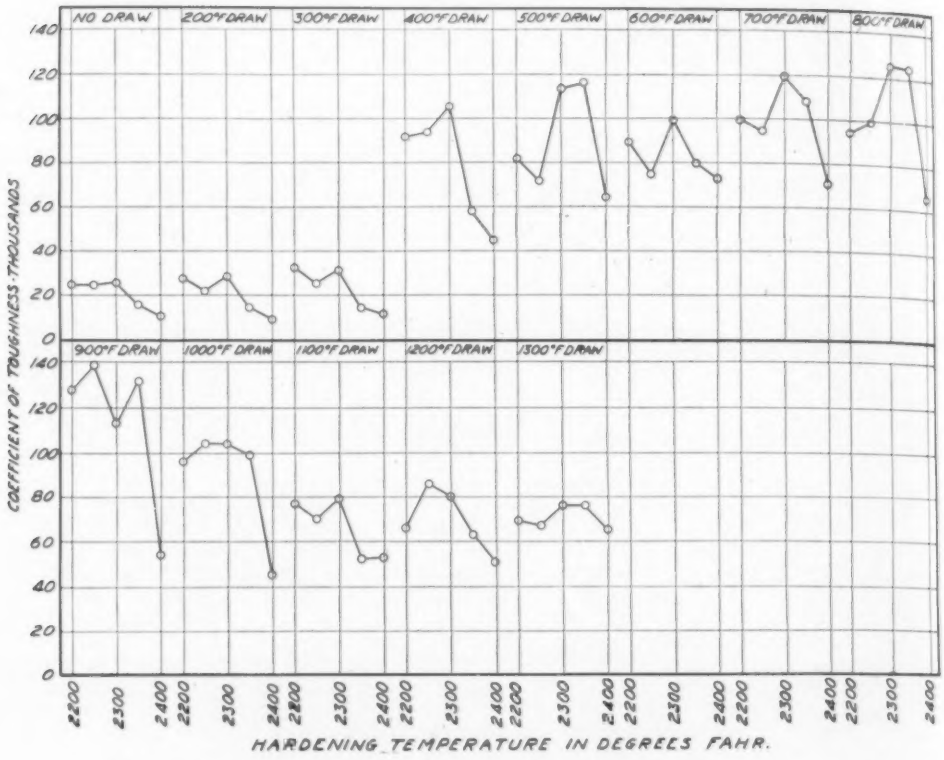

Fig. 38—Coefficient of Toughness Versus Hardening Temperatures.

of the matrix or the body of the austentic grains and its decomposition products.

Fig. 45 shows the matrix to be very resistant to etching attack, having only a faint trace of structure. The matrix in this specimen is believed to be composed of an intimate mixture of austenite and martensite in a fine state of division.

Fig. 43 shows more definite structural markings in the matrix. The portions of the matrix attacked by the etching, outline other resistant portions. It is believed that the easily attacked portions are areas of carbon-poor martensite which are changing to troostite. The portions resistant to attack are believed to be either austenite or carbon-rich martensite.

Fig. 46 shows stronger markings in the matrix than Fig. 43, otherwise they are much the same. It is believed that the carbon-poor primary martensite has now been largely converted to troostite. The austenite has probably not yet begun to decompose to secondary martensite.

Fig. 47 shows a marked change in the matrix. It has become

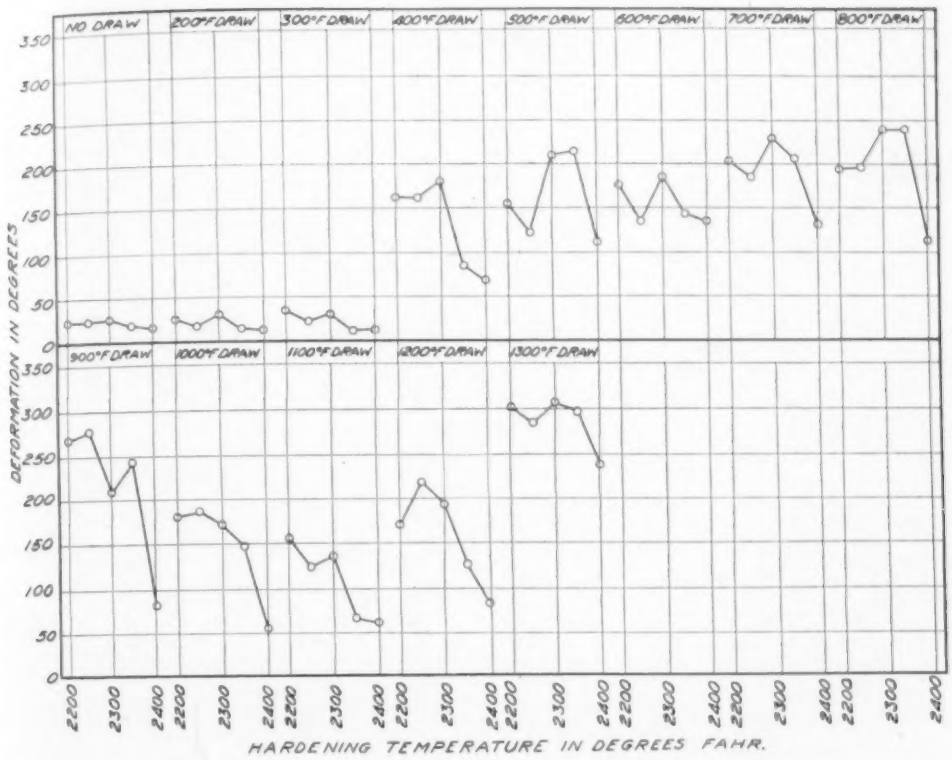

Fig. 39—Plastic Deformation Versus Hardening Temperatures.

much more easily etched. This change is believed to have been due to the breaking down of the austenite to secondary martensite and to the conversion of an increased part of the primary martensite to troostite. Many white areas probably of carbon-rich martensite remain. The outlines of the original austenite grains have become indistinct.

Fig. 48 shows a complete disappearance of the austenite grain boundaries. A large part of the matrix is now readily etched and probably consists of troostite, in some of which the carbides are arriving at the sorbitic particle size. The white portions of the matrix are believed to be carbon-rich martensite which is showing great resistance to decomposition.

Correlation of the Physical Properties

When comparison is made between the curves for the Rockwell hardness, the ultimate torque and the plastic deformation, it is obvious that there is no simple relation between them. Each curve has its own individually and appears to be recording a different effect of the

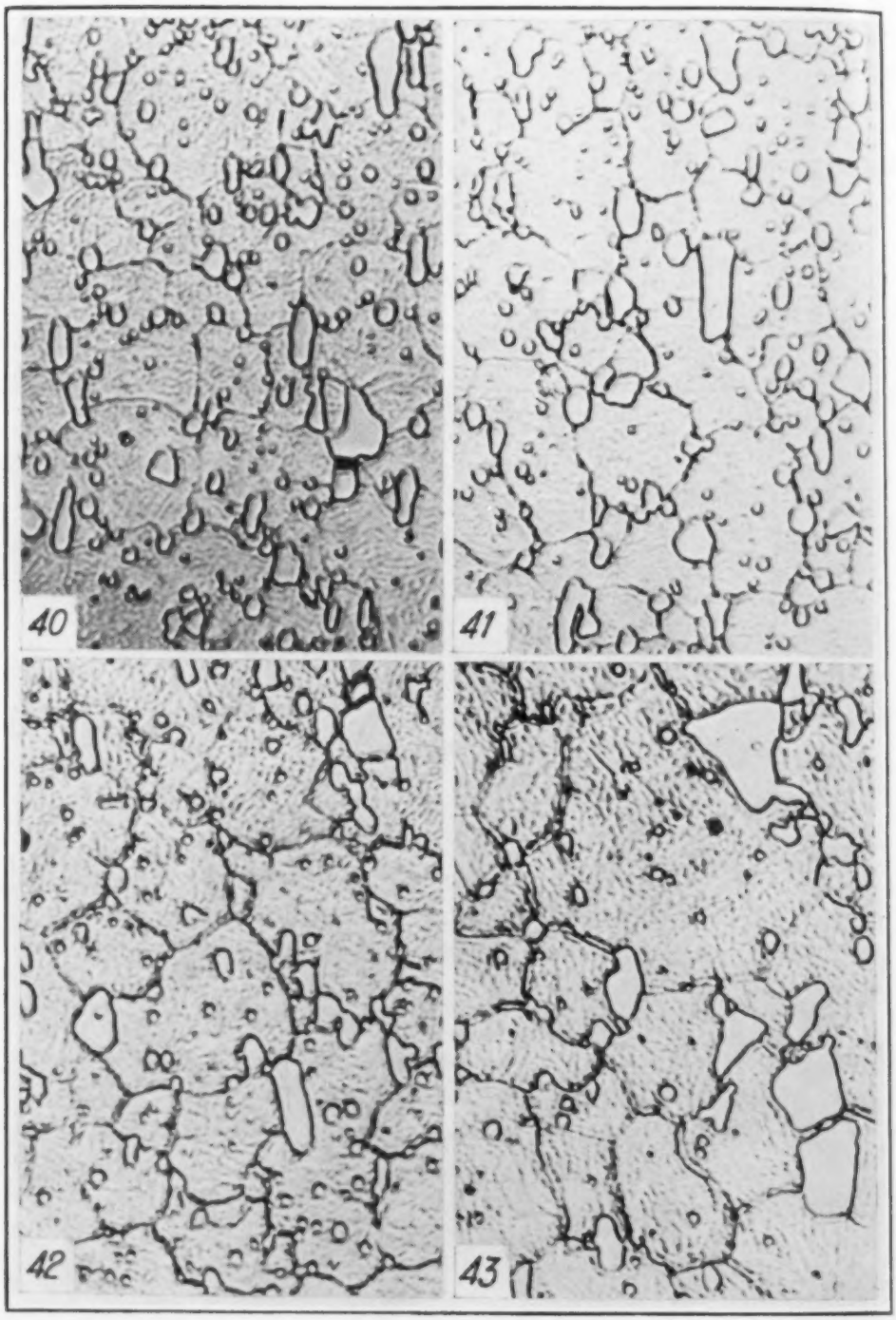

Fig. 40—High Speed Steel Hardened at 2200 Degrees Fahr. (1205 Degrees Cent.), Drawn at 400 Degrees Fahr. (205 Degrees Cent.), × 2000.

Fig. 41—High Speed Steel Hardened at 2250 Degrees Fahr. (1230 Degrees Cent.), Drawn at 400 Degrees Fahr. (205 Degrees Cent.), × 2000.

Fig. 42—High Speed Steel Hardened at 2300 Degrees Fahr. (1260 Degrees Cent.), Drawn at 400 Degrees Fahr. (205 Degrees Cent.), × 2000.

Fig. 43—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.), Drawn at 400 Degrees Fahr. (205 Degrees Cent.), × 2000.

changes in physical constitution upon the properties of the steel. Limited relations may be noted as follows: Hardness appears to be inversely proportional to strength from no draw up to the vicinity of the 600 degrees Fahr. (315 degrees Cent.) draw. Thereafter up to the 1300 degrees Fahr. (705 degrees Cent.) draw, it becomes proportional. Hardness and plasticity show inverse proportionality at the hardening temperature of 2400 degrees Fahr. (1315 degrees Cent.). At lower hardening temperatures this relationship becomes more doubtful.

Microstructure and the Physical Properties

If the dominant structural combinations are compared with their physical properties, interesting relationships are found. The structural forms, austenite, troostite and sorbite, are so well known that no further description is necessary. Martensite however exhibits several different variations which may be understood from the following outline of the formations observed in normally heat treated high speed steel such as is now being considered. As quenched the structure of the matrix is believed to consist largely of martensite with a considerable proportion of retained austenite. This martensite which is formed upon quenching is termed primary martensite. The primary martensite appears to consist of two varieties, one of which is converted to troostite at low drawing temperatures, while the other is very resistant to drawing. This varying susceptibility to drawing is believed to be due to the amount of carbon which the martensite contains. High carbon content renders the martensite more resistant to drawing, while low carbon content renders it more easily converted to troostite. When a high draw converts the retained austenite to martensite, this is called secondary martensite to distinguish it from the primary varieties. It is recognized that the structural changes involved in the decomposition of austenite into its various products, require a considerable amount of time. It is obvious that there are at times several constituents simultaneously undergoing change so that the structure may at any time represent different mixtures in indefinite proportions. For the purpose of comparison the structures have been roughly divided into four typical combinations which are named for their dominant constituents. An analysis of their physical properties is as follows:

Austenite and Primary Martensite, (Illustrated by Fig. 45).

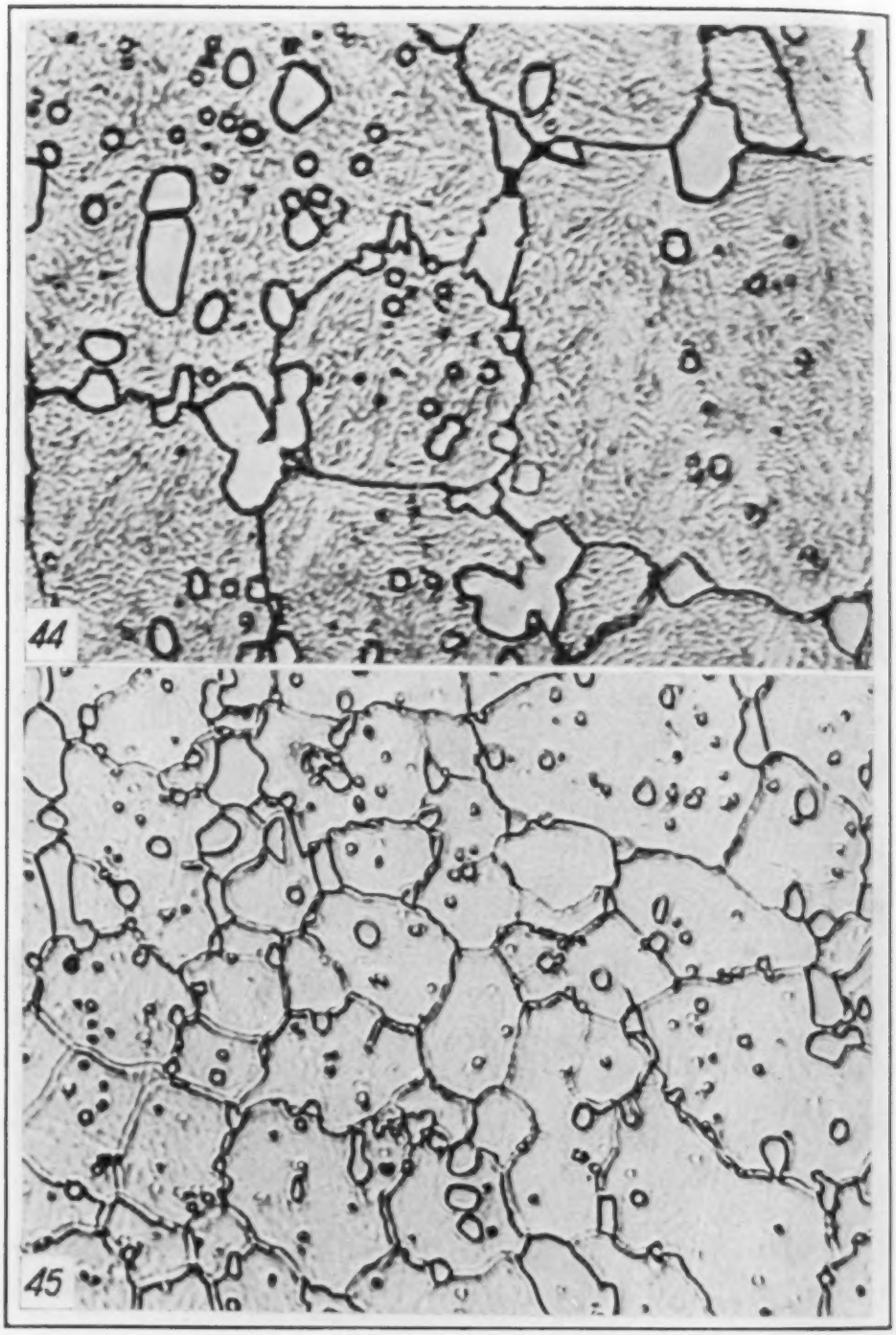

Fig. 44—High Speed Steel Hardened at 2400 Degrees Fahr. (1315 Degrees Cent.), Drawn at 400 Degrees Fahr. (205 Degrees Cent.), × 2000.

Fig. 45—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.) Not Drawn, × 2000.

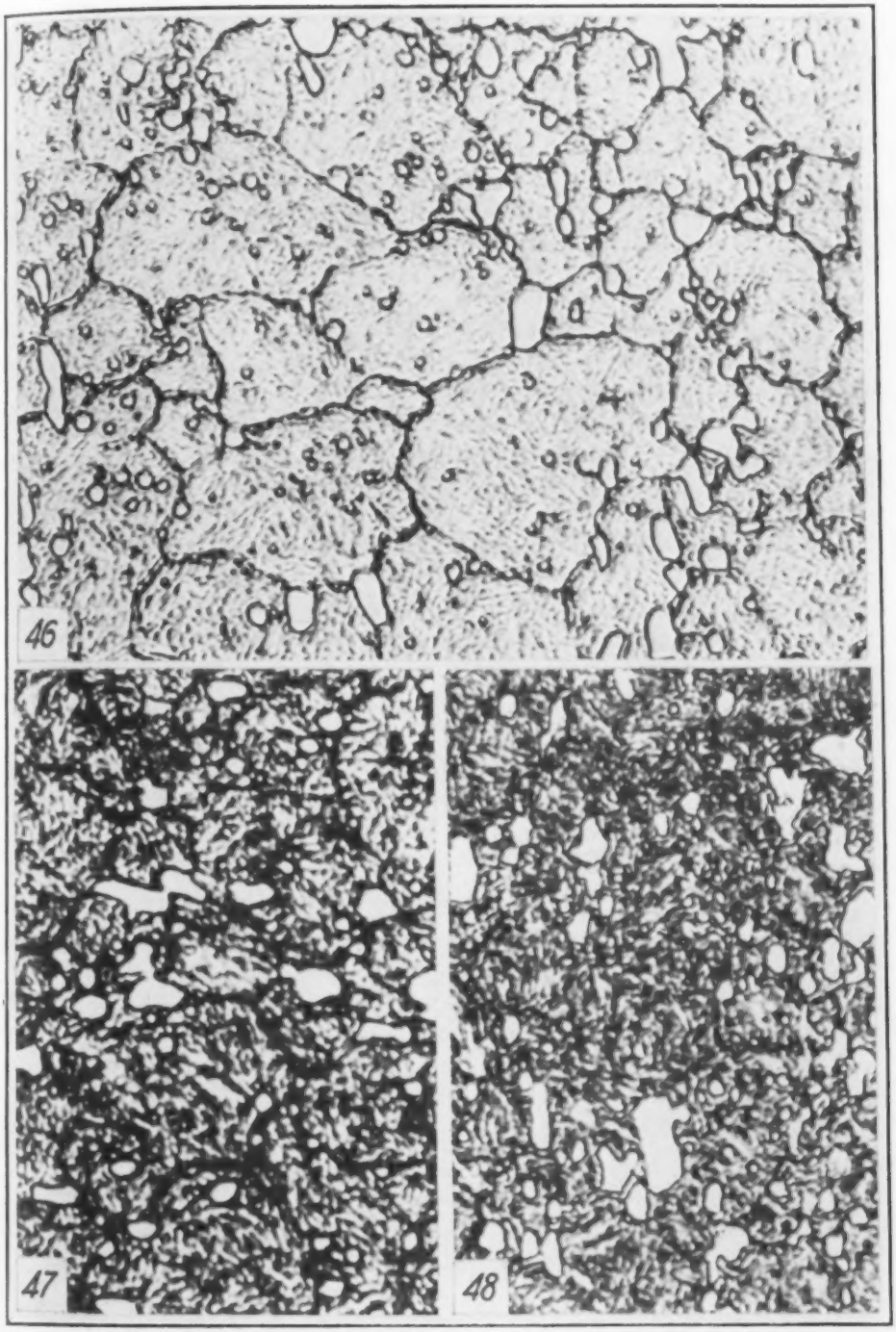

Fig. 46—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.) Drawn at 900 Degrees Fahr. (480 Degrees Cent.), × 2000.

Fig. 47—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.) Drawn at 1000 Degrees Fahr. (540 Degrees Cent.), × 2000.

Fig. 48—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.), Drawn at 1300 Degrees Fahr. (705 Degrees Cent.), × 2000.

This combination exists from no draw to a draw of about 300 degrees Fahr. (150 degrees Cent.). Its properties are briefly as follows:

Hardness, high, ranging from Rockwell C64 to C66.

Strength, moderate, showing an ultimate torque from 250 to 375 inch-pounds. The strength decreases with increased amounts of retained austenite.

Plasticity, very low, being below 50 degrees of twist.

Toughness, low, being particularly low at high hardening temperatures.

Austenite, Primary Martensite and Troostite, (Illustrated by Fig. 42).

This combination exists after drawing temperatures from about 400 degrees Fahr. (205 degrees Cent), to 800 degrees Fahr. (425 degrees Cent.). Its properties are summarized as follows:

Hardness, moderate, ranging from Rockwell C60 to C63.

Strength, high, showing an ultimate torque from 375 to 440 inch-pounds.

Plasticity, very high, ranging from 100 to 250 degrees of twist.

Toughness, very high, especially at the higher drawing temperatures of the range.

Secondary and Primary Martensite and Troostite (Illustrated by Fig. 47).

This combination exists after draws between 900 degrees Fahr. (482 degrees Cent.) and 1100 degrees Fahr. (595 degrees Cent.). Its properties are as follows:

Hardness, high, ranging from Rockwell C62 to C66.

Strength, very high, showing an ultimate torque from 400 to 475 inch-pounds. The strength developed in this structure is the highest observed in the experiment.

Plasticity, high at the lower draws of the range, but falling off sharply at the higher draws.

Toughness, very high in the vicinity of draw 900 degrees Fahr. (482 degrees Cent.), then falling off to moderate values with higher draws.

Secondary Martensite, Troostite and Sorbite (Illustrated by Fig. 48).

This combination exists after draws of 1200 degrees Fahr (650 degrees Cent.) and higher.

Hardness, low, being below Rockwell C60.

Strength, low, and falling with increasing draws.

Plasticity, moderate, and increasing with higher drawing temperatures.

Toughness, moderate, without definite trend.

Discussion

The question as to the exact nature of martensite or the mechanism of its formation from austenite will not be here considered. Some of the observations made are believed to throw additional light upon the existing theories.

Martensite resists etching and appears white in the photomicrographs here shown. The martensite does not assume an acicular or needle shape, but is more vermiform in appearance. It is believed that this vermiform martensite is formed in high speed steel when there is not sufficient time or freedom of atomic movement at the hardening temperature to permit the development of the familiar needles. The dark easily etched areas which outline the martensite "worms" are believed to be troostite which has been precipitated from carbon-poor primary martensite. The effect of the carbon content of the martensite upon its stability, is believed to be important. The distribution of the carbon in the martensite is affected by many causes such as the original distribution of carbide masses in the annealed structure and the time allowed for diffusion at the hardening temperature. It appears likely that many of the physical properties may be affected materially by the degree to which the martensite is saturated with the carbon and by the uniformity of its distribution. Martensite is the strong as well as the hard constituent of high speed steel. The greatest strength occurs when the secondary martensite is first formed and while the bulk of the primary martensite yet remains. Martensite has in itself a low order of plasticity, while its combination with austenite may show still less. This confirms observations made by De Long and Palmer[8] and by the writer[1] in connection with another type of steel, that some mixtures of austenite and martensite are particularly brittle.

Troostite appears to be the plasticizer which contributes to high speed steel this essential component of toughness. The formation of even slight amounts of troostite in the vermiform martensite, greatly increases the plasticity. The maximum plasticity occurs at the intermediate drawing temperatures when the troostite component is high while the secondary martensite has not yet begun to form. A principal cause of the low plasticity shown by the specimens hardened at 2400 degrees Fahr. (1315 degrees Cent.) would be the low troostite content due to the increased saturation of the martensite with carbon.

Summary of Conclusions

The response of the several physical properties to the variations of heat treatment has been so definite that confidence is felt that the picture presented of the behavior of the steel is a true one.

[8]B. H. DeLong and F. R. Palmer, "What Happens when High Speed Steel is Quenched," Transactions, American Society for Steel Treating, Vol. 13, 1928, p. 420.

A measurable amount of plasticity is demonstrated in hardened high speed steels at all heat treatments. The variations in the plasticity appear to be governed largely by the troostite content of the structure.

The strength of hardened high speed steel appears to be largely dependent upon the quantity and nature of the martensite present. The addition of a small quantity of troostite appears to aid the strength by supplying sufficient plasticity to permit a better distribution of the stresses.

Variations in the amount of carbon taken into solution produce three general types of martensite, first a primary type with low carbon content which is converted to troostite at low drawing temperatures, second a primary type with high carbon content which decomposes to troostite only at high drawing temperatures and third a secondary martensite resulting from the decomposition of austenite at high drawing temperatures.

A structure of martensite which appears to be distinct from the familiar needles, has been termed "vermiform martensite."

The indefinite property of toughness has been analyzed into its components of strength and plasticity and evaluated numerically. The result is regarded as useful in a practical way.

The hardness appears to be governed by the amount of martensite present. Austenite and troostite when present, act to lower the hardness.

These results upon a normal composition of high speed steel with a normal range of heat treatments are regarded as a basis of comparison for more extended investigation of the effect of other variations in heat treatment or in chemical composition.

Acknowledgments

The author expresses his appreciation of the assistance rendered by the laboratory staff of the Cleveland Twist Drill Co. Particular credit is due to A. S. Townsend for the photomicrographs and to L. W. Fraser for the charts and curves.

DISCUSSION

Written Discussion: By John A. Mathews, vice-president, Crucible Steel Company of America, New York City.

This paper, together with the one Mr. Emmons recently submitted to the

American Society for Testing Materials, are very interesting contributions to our knowledge of tool steels. Mr. Emmons has employed to very good effect the torsional method for obtaining information concerning the response of various materials to quenching and tempering. His figures show that the method may be considered dependable and that results can be reproduced. In the case of high speed steel, it would appear that the art of heat treatment has preceded the science, since the quenching temperatures of from 2300 to 2350 degrees Fahr. with a 1000 to 1100 degrees Fahr. draw are quite the usual practice. Under these particular conditions of treatment it will be noticed, as compared with as-hardened condition, we gain very materially by tempering in coefficient of toughness, torque and deformation. The hardness is approximately the same. It is evident that we do not customarily use high speed steel in the condition showing maximum coefficient of toughness but at approximately the maximum torque value. The intermediate drawing temperatures, such as 500 to 900 degrees Fahr., give a higher coefficient of toughness than practical experience indicates is necessary for the successful use of high speed steel; also the condition represented by the 1000 to 1100 degrees Fahr. draw indicates a much lower plastic deformation than is obtained in steel drawn at the intermediate points or hardened at lower temperatures. Nevertheless, the intermediate draws and lower hardening temperatures are seldom used.

There are still many tools used, particularly lathe tools, in which the temper is not drawn at all. The initial hardness of such tools is about the same as it is after the 1000 to 1100 degrees Fahr. draw but their coefficient of toughness, plastic deformation and torque are all much lower. When such tools give good service is it possible that the tempering within this range takes place spontaneously as a result of frictional heat, provided the edge does not crumble in the meantime? If Mr. Emmons wishes to put us under still greater obligation to him, I would suggest that he determine the torsional properties at elevated temperatures, particularly, from 900 to 1100 degrees Fahr. This might give us a great deal of useful information about the actual properties of the metal at the cutting edges when working under severe conditions.

Written Discussion: By Albert Sauveur, Gordon McKay professor of metallurgy and metallography, Harvard University, Cambridge, Mass.

Mr. Emmons' paper brings out the usefulness of the torsion test in determining the physical properties of steel. In this I unhesitatingly concur. We have used it for several years at the Harvard Engineering School with excellent results. There is much to be said in its favor when compared with the tensile test so universally employed. What the author designates as "coefficient of toughness," namely, the product of the ultimate torque by the ultimate deformation, that is, the stress by the strain, has been called by others, I believe, the "work of rupture," as it represents, roughly at least, the work required to produce rupture. I agree with Mr. Emmons that this may be considered an indication of the toughness of the steel.

Referring to the author's belief that the matrix of the steel quenched at 2350 degrees Fahr. (1285 degrees Cent.) and not drawn is an "intimate mixture of austenite and martensite in a very fine state of division," one would like to have some evidence in support of it. When it is considered that the excellent

photomicrograph (Fig. 45) illustrating this structure is magnified 2000 diameters and does not show any indication of the matrix being an aggregate the demand appears justified.

It is evident that the drawing operation produces changes in the matrix, while leaving the carbides undisturbed. One may, of course, speculate as to the nature of these changes. I am inclined to consider them as resulting from the decomposition of the austenite matrix which at the drawing temperature becomes unstable, at least when the steel is maintained at that temperature for some thirty minutes. The decomposition of austenite necessarily results in the formation of a new phase which may properly be called the "alpha phase." According to individual preference, it may also be called martensite or troostite. I also believe that this alpha phase has little solubility for carbon, carbides being precipitated in a fine state of division, and this adds to the cutting properties of the steel. It is generally described as secondary hardness.

The drawing of high speed steel does not differ in its essence from the tempering of hardened carbon steel. Both deal chiefly with the decomposition of retained austenite. In high speed steel, after the high temperature quench, we retain at room temperature substantially 100 per cent austenite. This austenite is relatively stable and requires for its decomposition high tempering (drawing) temperature. The retained austenite of quenched carbon steel, on the contrary, is more unstable and decomposes at considerably lower temperatures. In hardened steel, moreover, another constituent is present called martensite by many, which is likewise unstable and also undergoes decomposition.

Mr. Emmons deals at some length with the occurrence and behavior of martensite in high speed steel. I wish he had expressed an opinion as to the nature of this much discussed constituent. That it contains alpha iron is generally conceded, that some carbon is retained in solid solution in the alpha iron and that some carbide particles are also present seems highly probable. In what respect then does martensite differ from troostite? As martensitic needles result from the alpha phase forming along some crystallographic planes of the austenite, it is not easily understood why lack of time should produce martensite "vermiform" in appearance.

In view of the many varieties of martensite already reported, I cannot help regretting that the author has added to the list, namely, primary martensite subdivided into readily decomposable primary martensite and difficultly decomposable primary martensite, secondary martensite and vermiform martensite.

There is no doubt but that the results reported by Mr. Emmons should prove of much value to treaters and users of high speed. They will be appreciated and he should be warmly congratulated.

Written Discussion: By H. M. Boylston, professor of mining and metallurgy, Case School of Applied Science, Cleveland.

Whenever Mr. Emmons "takes his pen in hand" we know that we may expect something good, and the present paper is no exception to the rule. It seems to me that this collection of experimental data and the conclusions drawn from them should be of great value to the many users of high speed steel and can be accepted with a feeling of security as to accuracy and thoroughness. The author and his assistants are also to be congratulated upon the excellence of

their photomicrographs. In spite of the improvements made in photomicrographic apparatus in the last five years or so and the fine work of Lucas, Guthrie, Percy Hodge, Wobbe, Dennison and others, it is no simple matter to turn out photomicrographic work of the clearness and crispness of those in the present paper, which I note were all made at a magnification of 2000 diameters.

Written Discussion: By H. G. Keshian, metallurgist, Chase Companies, Waterbury, Conn.

Many methods of testing metals have been devised in an effort to directly measure certain characteristics, such as hardness, toughness, ductility, resistance to wear, impact, etc. These efforts, however, have not always been successful, particularly in those instances where the characteristics which we have endeavored to measure have not been easily amenable to direct measurement or where they could not be isolated from other properties for direct observation and study. In these cases we have tried to evaluate these properties in terms of other seemingly related and more easily measurable properties; but here again the results when applied to practical ends have not always been reliable. For instance, in the heat treatment operations we have generally assumed that hardness and toughness are inversely proportional, simply because of a lack of a dependable method of testing toughness; but Mr. Emmons has shown in his previous work on hardened tool steel that toughness and hardness bear no simple relation to each other.[1]

In the testing of metals for their physical properties, the true progress, therefore, appears to lie in the discovery of methods which more directly measure the properties which we want to measure, and Mr. Emmons' method of testing the toughness of hardened high speed steel as described in this paper certainly belongs to this class of work and to my mind is a distinct addition to our present scanty knowledge on the subject, and it is hoped that the direction in which he is carrying his investigation will become more and more general. As it has been my privilege to state on another occasion to this Society, there are few things in connection with the testing of tool steels that are so much valued by the consumer as to know in measurable form the properties of tool steel which he must apply to his various requirements.

Among many other important data brought out by Mr. Emmons there is one upon which I wish to add my suggestion. This pertains to the proper distribution of carbides in annealed high speed steel and their effect on its mechanical properties after hardening. In view of the large amount of work done in the metallographic study of high speed steel which has clearly shown the necessity of proper control of carbide distribution we still have to closely watch this condition in high speed steel which is worthy of the thought of those who have a good deal to do with final structural condition of the metal before it leaves the steel mill.

Written Discussion: By S. C. Spalding, metallurgist, American Brass Co., Waterbury, Conn.

I have read Mr. Emmons' paper with a great deal of interest, as it adds new experimental data to the mysterious and interesting properties of hardened

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[1] J. V. Emmons, "Some Physical Properties of Hardened Tool Steel," *Proceedings* of American Society for Testing Materials, Vol. 31, 1931, p. 47.

high speed steel. I believe it is quite commonly considered that the best treatment to develop maximum red hardness and cutting qualities is to quench at 2350 degrees Fahr. and draw at 1050 to 1100 degrees Fahr.

Mr. Emmons' torsion tests show that at this point we are at the point of maximum strength in torsion. The figure called plastic deformation is not a maximum at this point—in fact, it is higher at draws of 400, 700, 800 and 900 degrees Fahr., which results in the coefficient of toughness which is the product of strength and plasticity being greater also at these temperatures. I feel that there is a considerable risk involved in naming a product such as this coefficient of toughness. Toughness is a somewhat indefinable term, but I believe an average conception of it is ability to deform without or before breaking. If we accept that as the case, then would not the steel drawn at 1200 and 1300 degrees Fahr. be tougher than that at 900 degrees Fahr.? I also feel that in many tools of appreciable size and variable shapes that with the customary 2350-1050 degrees Fahr. treatment, the tools would be less liable to breakage in use than with a 400, 700, 800 or 900 degrees Fahr. draw. This may be due partly to better relief from internal strains from quenching with this treatment, which strains might not exist in a small diameter symmetrical piece such as used in these tests. I believe many of us have been called upon to diagnose tool failures by breaking, cracking, etc., and if the structure on examination was like that in photomicrographs 43, 45 or 46, we would say that the tool had been insufficiently drawn, hence was brittle, or lacked toughness and consequently broke or cracked. Whether this effect was due to the underdrawn structure or to insufficient relief from internal strains or what, I do not know, but I do thoroughly believe it exists. I also believe and have seen demonstrated many times, that if another tool were made up from the same steel and quenched at 2350 degrees Fahr. and drawn at 1050 to 1100 degrees Fahr. it would perform without breaking. I do not wish to throw any doubt on the tests or values reported in this paper as I believe they were carefully performed and accurately recorded. I also believe that they throw valuable light on some of the structural happenings of high speed steel. I would wish to caution against their use as a criterion for the hardening of general high speed tools as I believe that the standard treatment of 2350-1050-1100 degrees Fahr. is still the best and that better efficiency and greater freedom from breakage of tools will result from this treatment than from one comprising draws of 400, 700, 800 or 900 degrees Fahr. which might be taken from the paper as more desirable.

Written Discussion: By A. H. d'Arcambal, consulting metallurgist, Pratt and Whitney Co., Hartford, Conn.

All manufacturers and large users of high speed steel should carefully read Mr. Emmons' excellent paper on this subject. In the writer's opinion this paper on high speed steel is one of the finest, if not the best, paper ever presented before our society on this important subject.

We have long desired information as to the effect of various heat treatments on the toughness of high speed steel. The results obtained from Mr. Emmons' carefully conducted torsional tests are very enlightening, the data being presented in splendid form.

The author finds that hardened high speed steel of the 18-4-1 type possesses

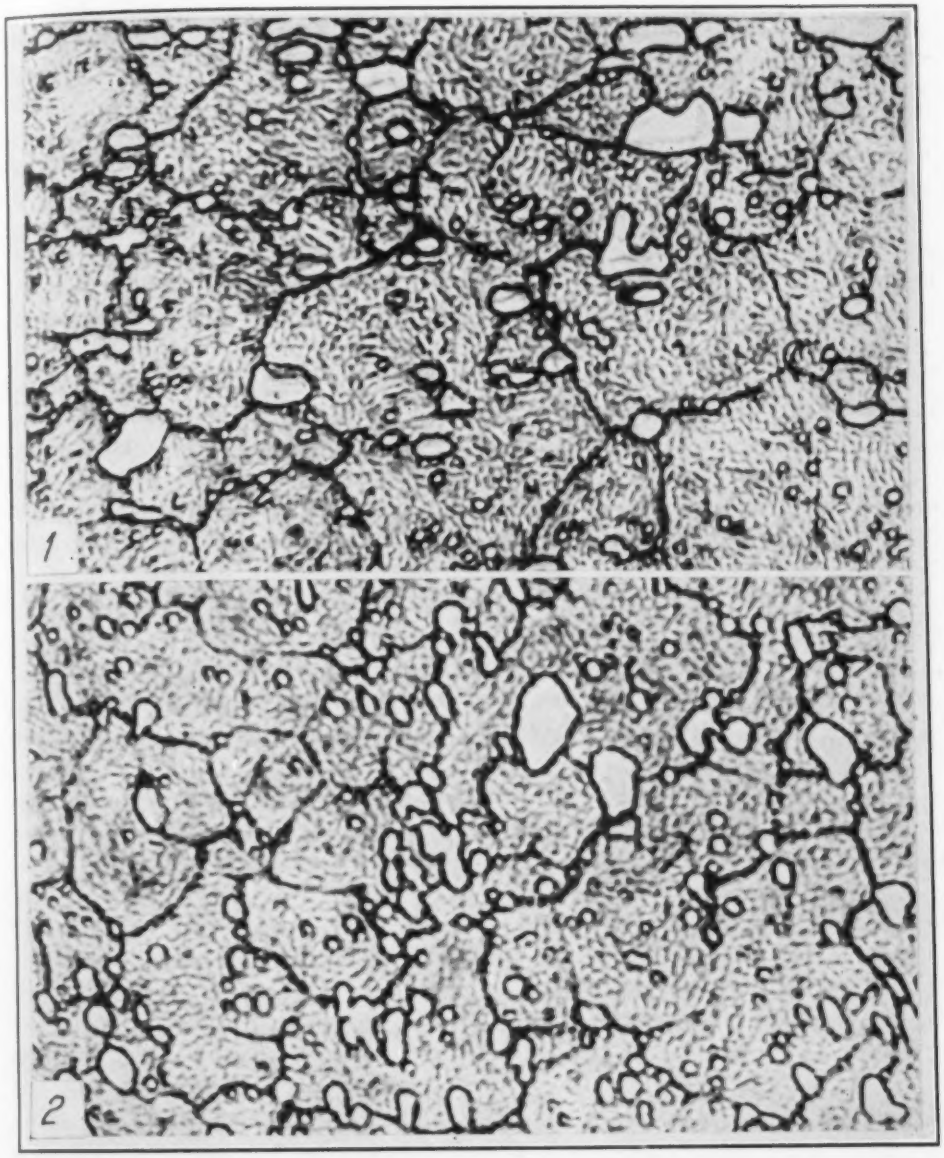


Fig. 1—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.) in Salt Bath being Soaked for 30 Seconds. Quenched in Oil. Drawn for 30 Minutes at 500 Degrees Fahr. × 2000.

Fig. 2—High Speed Steel Hardened at 2350 Degrees Fahr. (1285 Degrees Cent.) in an Electric Muffle being Soaked for 15 Seconds. Quenched in Oil. Drawn for 30 Minutes at 500 Degrees Fahr. × 2000.

the highest degree of toughness when drawn in the neighborhood of 900 degrees Fahr., thus closely checking the results obtained by previous investigators. While the so-called toughness factor is an important one in relation to the performance of the high speed steel tool, other equally important factors must be considered. Should we consider the toughness factor alone, one of the first questions that might be raised after noting the results in Table V would be—

"Why not harden high speed steel tools by quenching from 2200 to 2250 degrees Fahr. and drawing to 900 degrees Fahr., instead of employing a higher temperature of say 2350 degrees Fahr., followed by a 900 degrees Fahr. draw? This treatment results in almost as high a coefficient of toughness as obtained when quenching from the higher temperatures and there is less liability of losing the tools due to excessive scaling, etc." The answer to this question is that tools should be quenched from the highest possible temperature short of coarsening of the grain due to the greater amount of the excess iron-tungsten carbide dissolved in the austenitic matrix at the higher temperature. One then might question the general practice of drawing high speed steel tools such as drills, reamers, cutters, hobs, taps, etc., to 1050 to 1150 degrees Fahr. after quenching from 2350 degrees Fahr. when much greater toughness is obtained by drawing to only 900 degrees Fahr. We believe the reason for high speed steel metal cutting tools giving superior performance when drawn at the higher temperature at the expense of toughness is due principally to the greater number of extremely minute iron-tungsten carbide particles (submicroscopic) precipitated out at this higher drawing heat. It might also be stated at this time that the demand today is for high speed steel tools possessing a high degree of hardness (Rockwell C 63-65) as well as being file hard due to the harder and tougher material being fabricated than was the case a few years ago. The 900 degrees Fahr. draw after the proper quench results in a lower Rockwell reading than is obtained from the higher drawing treatment, specimens after the 900 degrees Fahr. draw, moreover, being easily filed, as compared with file hardness obtained after the 1050 degrees Fahr. draw.

Mr. Emmons proves conclusively that the Rockwell hardness on a high speed tool does not indicate the toughness of the same. Just add another column to Table V, this column showing the Rockwell hardness, then note the varied toughness readings for the same Rockwell hardness.

The author has also clearly shown that the Rockwell hardness obtained on all of the specimens as quenched is practically the same whether the specimen is quenched from 2200 or 2400 degrees Fahr. This confirms the results obtained from time to time by the writer but is in disagreement with recent trade journal articles by other investigators.

Mr. Emmons states that a mixture of martensite and austenite has less plasitcity than martensite itself. Should we not therefore expect a higher order of plasticity after the 1000 degree Fahr. draw than was obtained from the 900 degrees Fahr. draw, considering that practically all of the austenite is converted to martensite at the 1000 degrees Fahr. temperature?

We also believe that primary martensite exists to some extent after a draw as high as 1250 degrees Fahr. should the quenching temperature be 2350 degrees Fahr. or higher, due to the Rockwell hardness obtained. There can be only a small amount of secondary martensite present considering that high speed steel as quenched has so little austenite.

The author used the salt bath for hardening his specimens. Considering that the so-called open fire method is commonly employed for hardening high speed steel tools, we suggested to Mr. Emmons that he prepare twelve more specimens from the same coil of wire if possible, these specimens to be hard-

ened in one of our electric globar high speed steel furnaces. As the original coil of wire was used up, Mr. Emmons prepared 24 additional specimens from a coil of almost identical analysis, sending 12 to Hartford for treatment. These 12 specimens were quenched from 2350 degrees Fahr., being allowed to remain in the furnace 15 seconds after the small diameter of the specimen came to heat. Four of these specimens were then drawn to 500 degrees Fahr. in oil for 30 minutes at temperature, four more specimens were drawn in lead at 900 degrees Fahr. for 30 minutes at heat, the remaining specimens being drawn at 1100 degrees Fahr. for 30 minutes in lead. The remaining 12 specimens were hardened by Mr. Emmons in the same manner with the exception of using the salt bath instead of the box type furnace, as well as soaking the specimens for 30 seconds as compared with our 15 second soak.

The results obtained from the specimens hardened in the electric muffle furnace compared quite favorably with the salt bath treated specimens. The principal difference observed was that the specimens hardened in the electric furnace were slightly lower in Rockwell hardness and possessed greater plasticity than the samples hardened in the salt bath. Considering that the electric muffle furnace specimens were allowed to soak at the hardening temperature only 15 seconds as compared with the 30-second soak given the salt bath treated specimens, explains this slight difference. It was gratifying to note that both methods of hardening gave practically the same results. The photomicrographs of the specimens given the 500 degrees Fahr. draw are shown in Figs. 1 and 2 of this discussion. The specimen treated in the salt bath furnace had a slightly larger austenitic grain size than the electric furnace treated specimen as would be expected from the soaking time.

Undoubtedly this splendid paper will result in similar tests being conducted by other investigators studying high speed steel. We sincerely trust that the author will continue this work on the physical properties of high speed steel, noting the effect of varying percentages of carbon on the physical properties of high speed steel as well as studying the effect of different times at the hardening and drawing temperatures, etc.

Written Discussion: By O. W. Ellis, director of metallurgical research, Ontario Research Foundation, Toronto, Canada.

Through the courtesy of Mr. Emmons, the writer was given opportunity to test the entire series of samples investigated by him, using the Vickers hardness testing machine which employs as the indenting tool a diamond pyramid having an included angle of 136 degrees. The use of an indenting tool of this design is justified by the fact that the hardness numbers obtained coincide closely with the standard Brinell hardness numbers which would be obtained on the same material if balls having no tendency to distort under load could be employed in making the Brinell impressions.

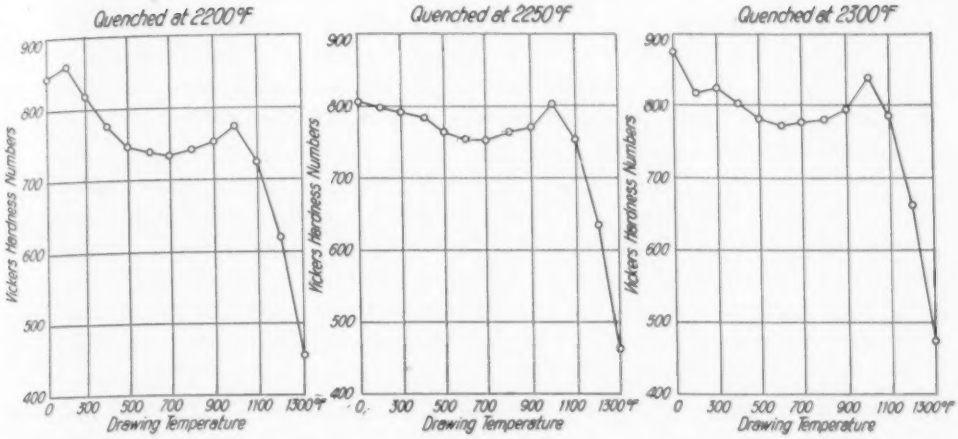
The figures shown in Column 8 of the following table, which is headed "General Average," are the averages of six determinations made on each of three specimens, all of which had been treated by Mr. Emmons under as nearly identical conditions as possible.

The values in Column 8 are the Vickers numbers corresponding to the Rockwell numbers in Column 8, Table VI, of Mr. Emmons' paper.

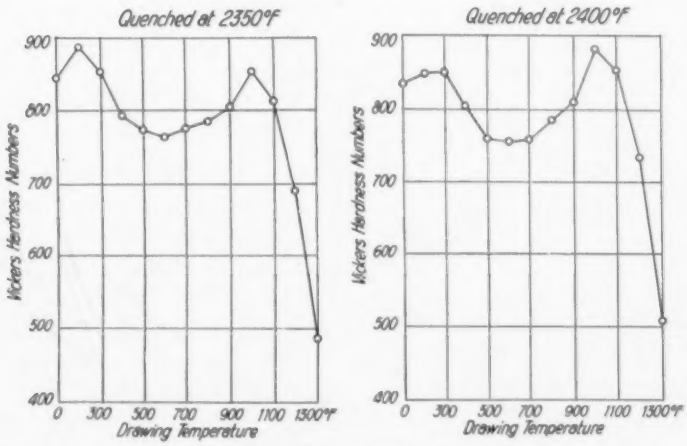
Vickers Hardness Determinations, Using 10-Kilogram Load

Heat Treatment: Hardening Temperatures Deg. Fahr.	Hardening Temperatures Deg. Cent.	Drawing Temperatures Deg. Fahr.	Drawing Temperatures Deg. Cent.	Averages of 6 Determinations on Each Specimen			General Average
2200	1205	No Draw	...	884	782	870	845
		200	95	881	886	813	860
		300	150	828	838	791	819
		400	205	781	770	777	776
		500	260	743	754	746	748
		600	315	740	740	739	739
		700	370	735	734	728	732
		800	425	745	741	737	741
		900	480	753	753	753	753
		1000	540	772	773	770	772
		1100	595	723	731	723	726
		1200	650	620	625	616	620
		1300	705	471	448	452	457
2250	1230	No Draw	...	804	803	810	806
		200	95	809	761	828	799
		300	150	734	813	827	791
		400	205	778	793	779	783
		500	260	765	762	763	763
		600	315	757	754	755	755
		700	370	748	756	757	754
		800	425	763	763	766	764
		900	480	769	771	771	770
		1000	540	801	801	804	802
		1100	595	757	751	751	753
		1200	650	633	636	633	634
		1300	705	466	463	461	463
2300	1260	No Draw	...	845	882	901	876
		200	95	776	827	850	818
		300	150	812	845	811	823
		400	205	801	811	793	802
		500	260	782	781	781	781
		600	315	775	768	776	773
		700	370	776	779	777	777
		800	425	778	780	781	780
		900	480	796	793	800	796
		1000	540	840	839	837	839
		1100	595	785	785	792	787
		1200	650	659	659	664	661
		1300	705	473	472	475	473

Heat Treatment: Hardening Temperatures Deg. Fahr.	Hardening Temperatures Deg. Cent.	Drawing Temperatures Deg. Fahr.	Drawing Temperatures Deg. Cent.	Averages of 6 Determinations on Each Specimen			General Average
2350	1285	No Draw	...	839	839	864	847
		200	95	887	887	886	887
		300	150	850	858	856	855
		400	205	794	794	784	793
		500	260	772	777	775	775
		600	315	764	763	760	766
		700	370	778	779	772	776
		800	425	787	787	783	786
		900	480	806	804	798	803
		1000	540	853	853	857	854
		1100	595	813	809	814	812
		1200	650	691	692	689	691
		1300	705	482	480	496	486
2400	1315	No Draw	...	805	839	861	835
		200	95	830	857	859	849
		300	150	855	848	844	849
		400	205	803	802	802	802
		500	260	744	775	765	760
		600	315	758	757	752	756
		700	370	757	759	763	760
		800	425	782	781	793	785
		900	480	812	814	804	810
		1000	540	787	882	888	883
		1100	595	854	856	849	853
		1200	650	732	738	737	736
		1300	705	502	508	510	507



Figs. 1 to 3



Figs. 4 and 5

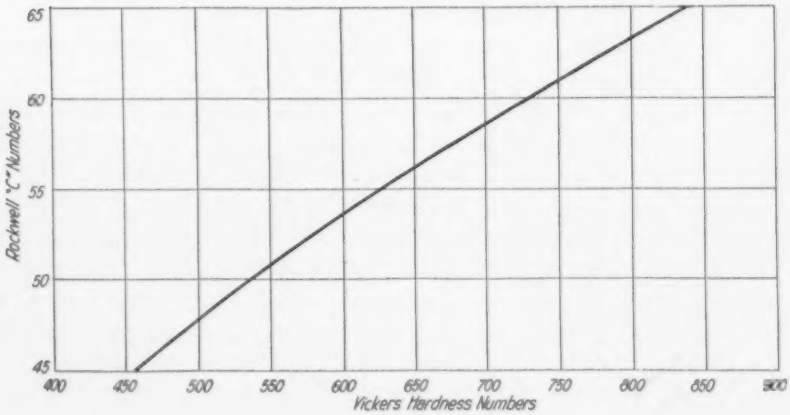


Fig. 6

February

General Average
845
860
819
776
748
739
732
741
753
772
726
620
457
806
799
791
783
763
755
754
764
770
802
753
634
463
876
818
823
802
781
773
777
780
796
839
787
661
473

General Average
847
887
855
793
775
766
776
786
803
854
812
691
486
835
849
849
802
760
756
760
785
810
883
853
736
507

In Figs. 1 to 5 (this discussion) are shown graphically the results quoted in Column 8 of the foregoing table. These correspond to Figs. 16, 20, 24, 28 and 32, respectively, of Mr. Emmons' paper. There is general agreement between the forms of Mr. Emmons' curves and those shown above, though some definite differences are to be observed.

Fig. 6 has been prepared with the view of showing the relationship between the Rockwell numbers and the Vickers numbers over the range 45-65 Rockwell. It is based in part on the results obtained by Mr. Emmons and myself and in part on results obtained earlier by myself on a series of samples of high speed steel from another source. It is worthy of note that Mr. Emmons' Rockwell hardness numbers fall very closely on the curve which I had previously prepared as the result of my own experiments.

One point which should be referred to in view of its importance is that the relationship between the Rockwell and Vickers numbers over this range of Rockwell numbers differs quite appreciably from the relationship shown on page 443-A of the National Metals Handbook (1930 Edition) between Rockwell numbers and Brinell numbers. The following table brings this point out quite clearly.

Rockwell (C)	Brinell* (3000 kg.)	Vickers (10 kg.)
45	430	456
50	488	535
55	548	626
60	613	730
65	...	838

In regard to the conversion table printed on page 433-A of the National Metals Handbook, it is stated that "it cannot as yet be freely recommended for use with tungsten high speed steels." The above table shows quite clearly, I feel, that this contention is justified, and that the suggestion that the conversion table in the National Metals Handbook is fairly correct falls rather outside the facts—that is, if we assume that the Vickers numbers represent what the Brinell numbers would be if no distortion of the ball occurred during test.

In concluding this discussion, I wish to express my wholehearted appreciation of the assistance given me in this work by Mr. Desmond Hunter.

Written Discussion: By R. K. Barry, foreman, heat treating department, Barry Company, Muscatine, Iowa.

The society is fortunate in having presented to it such a comprehensive study of the physical properties of high speed steel after various hardening and drawing treatments. The subject is an intriguing one that leads the investigator on and on into labyrinths seemingly without end.

The author's decision to soak all specimens for 30 seconds after they had reached the several hardening heats used, raises a doubt in my mind for we must presuppose the same rate of heating regardless of temperature, or in other words the rate is considered to be a constant even with other variations in evidence.

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*Values taken from conversion table on p. 433-A, National Metals Handbook (1930 edition).

The use of a salt bath as a heating medium was a wise choice, for decarburization is an important thing to avoid when working with small specimens. The choice of high speed steel drill rod as the test material pleased me, for I had urged further investigation with that material some years ago. The charts showing the stress-strain curves, together with the method used to determine the plastic, elastic, and total deformation are particularly interesting and in connection with them, special attention should be given to the fact that the slopes of the lines of proportionality are uniform.

It will be observed that the toughness values are low after drawing to 600 degrees Fahr., which is in agreement with our slow bend tests. One exception, however, is noted, i. e., hardening at 2400 degrees Fahr. with a 600 degrees Fahr. draw produces the highest coefficient of toughness (See Table V).

The coefficient of toughness is generally higher after a 900 degrees Fahr. draw than it is after drawing to 1000 degrees Fahr. Impact tests indicate a similar condition.

The Rockwell values shown in Table VI are normal and indicative of a high degree of accuracy all around.

What significance can be attached to the condition shown in Fig. 36, as follows: Specimens hardened at 2300 degrees Fahr. were harder after drawing to 500 degrees, 600 degrees and 700 degrees Fahr. than when hardened at 2400 degrees Fahr. Is grain size the answer?

The closeness of values shown in Tables II, III and IV from which the averages were computed, are particularly impressive.

Those who have studied or will study the figures in detail, will appreciate the beauty of the results from the standpoint of consistency and precision and that the whole research has depended to a large extent upon the technique used by Mr. Emmons in giving us such an excellent piece of work.

Author's Closure

The author is much indebted to those who have contributed to the discussion of this paper and especially to those who have done experimental work for the better development of particular points.

It should perhaps be made clearer that the variations in heat treatment under observation in this paper fall primarily in the range which is actually used for cutting tools. The exaggerated, clearly resolvable structures which may be developed for the purpose of microscopic study have been outside the scope of these experiments.

It should also be clearly understood that only a few of the variables which enter into the practical heat treatment of tools have been here considered. Any attempt to apply these results to tool hardening practice must be done with the understanding that information on the effect of variations in such factors as, composition of the steel, size of the tool, soaking time at high temperatures, quenching speeds, etc., is not yet available.

The kindly comments of Dr. Sauveur are especially appreciated. In reply to his inquiry as to the evidence in support of the statement that "the matrix of the steel quenched at 2350 degrees Fahr. (1285 degrees Cent.) and not drawn is an intimate mixture of austenite and martensite in a fine state of division," it

may be said that the general structure of Fig. 45 may be called typically austenitic. There are small faint markings visible in the matrix indicative of the vermiform type of martensite. These may be detected by close examination of some of the grains in the lower left hand corner of Fig. 45. The hardness is high (Rockwell C 64.9) which is indicative of martensite. The specimen is quite magnetic which indicates a high content of alpha iron or martensite. It was therefore considered that there must be a large amount of martensite present intermingled with the austenite and difficultly distinguishable from it.

The "alpha phase" so well defined by Dr. Sauveur as being the first product of the decomposition of austenite is the "martensite" described in the paper. It may or may not be able to assume a needle structure according to the time and degree of freedom of atomic movement present. It is believed from the evidence in these experiments that quenched high speed steel before the draw already contains a large percentage of this alpha phase or martensite, and that some of this primary martensite is more easily decomposed by drawing than the retained austenite.

As to the difference between martensite and troostite, the recent results reported by Jeffries,[9] Heindlhofer and Bain,[10] Öhman,[11] Sekito,[12] Ellinger[13] and others, give much information as obtained on carbon steel. The results of similar investigations of hardened high speed steel by means of X-ray and magnetic analysis are as yet lacking, but it is hoped that they will soon be available. The physical properties under observation in this paper show something of the behavior of these constituents but furnish no direct evidence as to their composition. From the evidence in this paper it may be said that:

> Martensite in high speed steel is hard and strong. It has very low plasticity. It resists etching by nitric acid. It may appear either acicular or vermiform according to the conditions present at the time of its formation. It occurs sometimes in the matrix of typical austenite grains in relatively small masses and is hardly to be distinguished microscopically from the retained austenite. Its composition does not appear to be uniform as some of it is easily decomposed to troostite while other portions are very resistant.
>
> Troostite in high speed steel is less hard and less strong than martensite. It is much more plastic. It etches dark with nitric acid. It does not appear to be present in freshly quenched high speed steel. As the steel is

[9]Dr. Zay Jeffries, "A Contribution to the Theory of Hardening and the Constitution of Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 13, 1928, p. 369.

[10]K. Heindlhofer and E. C. Bain, "A Study of the Grain Structure of Martensite," TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 673.

[11]Einar Öhman, "X-Ray Investigations on the Crystal Structure of Hardened Steel," *Journal*, Iron and Steel Institute, Vol. CXXIII, 1931, p. 445.

[12]Sinkiti Sekito, "On the X-Ray Analysis of the Cementite Obtained by Tempering Quenched Steels," Science Reports of the Tohoku Imperial University, Series I, Vol. XX, No. 2, 1931.

[13]G. A. Ellinger, "Thermomagnetic Investigation of Tempering of Quenched 0.75 Per Cent Carbon Steel," American Society for Steel Treating, Boston Convention paper. To be printed later in TRANSACTIONS.

drawn at increasing temperatures it starts to form at about 400 degrees Fahr. (205 degrees Cent.). Its first appearance is at the boundaries of the martensite.

The vermiform appearance of martensite might also be called "distorted martensite." The time element enters into its formation because the limited freedom of atomic movement in the austenitic solid solution makes crystallization and the development of slip planes slow. If there is but little freedom of movement and the time is short the result is imperfect slip planes, with the later formation of imperfect and distorted martensite needles along them. This distortion and imperfect development of the martensite needles may perhaps be a contributing factor to the great strength displayed by this type of structure.

The subdivision of martensite into different varieties showing different behavior is believed to be helpful to a better understanding of the effect of the variations in heat treatment commonly employed for cutting tools. It is recognized that the primary and secondary martensites of varying degrees of carbon content are only names for various typical stages of the progressive decomposition of austenite.

The observation made by Dr. Mathews that high speed steel is customarily used at the maximum torque value and not at the maximum of either toughness or hardness, is correct. High speed steel at its maximum toughness may be so low in hardness or strength as to limit its usefulness. This point is also brought out in Mr. d'Arcambal's and in Mr. Spalding's discussion.

It is hoped that it will be possible to extend the investigation to include the properties at elevated temperatures at some time in the future.

In response to Mr. d'Arcambal's inquiry it may be said that the mixtures of austenite and martensite which have been observed to be unusually brittle have been freshly quenched specimens, not drawn. The difference between the plasticity of such mixtures and that of martensite with little or no austenite is only slight. There is some evidence that the extreme brittleness noted may be due to more perfect development of the austenitic slip planes rather than to the mere presence of a mixture of the two constituents.

The experiment reported in Mr. d'Arcambal's discussion shows that there has been no considerable change in the physical properties due to the use of a different steel of similar analysis. Also, it is shown that the two methods of heating for hardening produced similar physical properties and similar microstructures. The author is grateful to Mr. d'Arcambal for his efforts in developing these valuable points.

The contribution of Dr. Ellis in checking the hardness determinations upon the Vickers machine is of great value both in confirmation of the author's hardness results and in the general information it gives as to the correlation of results by the two hardness testing methods. It is gratifying to know that the hardness results reported in the paper check so closely with those in Dr. Ellis' independent experiments. The comments in regard to the data in the handbook are referred to the Recommended Practice Committee for their consideration.

In reply to Mr. Spalding's comments in regard to the property of "toughness," it is the author's opinion that "toughness" is the ability to resist breakage,

which concept involves both strength and plasticity. It is agreed that the structures shown in photomicrographs 43, 45, and 46 are evidence of too low a draw for the best service in cutting tools. It should be noted that these structures all exhibit strengths below the maximum. Mr. Spalding's warning that "toughness alone is not a safe criterion for hardening high speed tools," is well taken.

In response to Mr. Barry's question in regard to the rate of heating, every effort was made to keep this constant. The reason for the peculiarity shown in Fig. 36, in that for the 500, 600 and 700 degrees Fahr. draws, the hardness is higher when hardened at 2350 degrees Fahr., than when hardened at 2400 degrees Fahr., may lie in the amount of retained austenite present.

The remarks of Mr. Keshian in regard to the necessity of proper control of carbide distribution, are so true that they cannot be too often repeated. In this experiment every effort was made to eliminate this condition as a variable. The author is pleased that Mr. Keshian regards this paper as being a step toward the solution of the problems of the consumer of tool steel, as so well stated in his recent paper before the society.

The comments of Professor Boylston as to the experimental work and the photomicrographs, are much appreciated as coming from so great an authority on the subject.

There are many peculiarities in the curves shown in the paper for which the explanations are yet lacking. It is hoped that future accessions of knowledge of the nature and behavior of high speed steel will enable these gaps to be filled in. It should be reiterated that hardened high speed steel is such a heterogeneous material, that many things are going on at the same time, whenever there is sufficient freedom of atomic or molecular movement to permit changes to take place. The physical properties as here measured are only the summation of the properties of the several structural units present at that particular time.

PRECIOUS METAL ALLOYS

By R. C. Brumfield

Abstract

There are a number of precious metal alloys which embody good possibilities for structural service through the wide range of properties obtainable, their corrosion resistance, and their possibilities of heat treatment. These alloys are described as to alloying elements and variations in percentages of these elements together with resulting properties.

Possibilities of heat treatment and reasons for heat treatment are discussed. Copper and gold probably affect heat treatment most. Methods of heat treatment are described. Some effects of variation in heat treating methods are discussed. Some data on permanency of properties are given.

Methods of testing are described as standardized by a group of interested manufacturers. A strain gage for making tensile tests and apparatus for making torsion tests are shown. A modified Johnson's apparent elastic limit is described which has certain advantages. A partial bibliography is included.

A GREAT number of alloys of wide variety are used by the dental profession for making structures required to serve definite purposes in the mouth. Tiny structures of these materials carry loads of surprising amount under such conditions that the material is required to meet severe demands as to workability, strength, flexibility and toughness. The demand by the dental profession for high service possibilities in the metal from which their structures are made, arises from the limited space in which the structure must operate, a desire to lighten weight for the comfort of the patient and, in many cases, a lack of adequate structural information on the part of the constructor of the appliance.

The constant pressure of these demands has promoted a continuous and intensive effort in the development of the alloys used.

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, R. C. Brumfield, is a member of the society. He is assistant professor of Civil Engineering at Cooper Union in charge of materials and hydraulics laboratories, New York City. Manuscript received June 2, 1931.

This has resulted in a bewildering number and variety of alloys available to the dental profession, with a range of properties wider than that available to almost any other user of structural material. The development of these alloys has taken two distinct directions, first a search for new alloys, offering improved possibilities for service, second, and more recent, efforts to improve existing alloys by careful attention to detail of manufacture, routine inspection testing and careful research testing of the metals.

There is very little knowledge of these alloys outside their field of usefulness. They have high service qualities, however, which would recommend them for use outside the field of dentistry in such places as the construction of fine machinery where resistance to corrosion and high strength are necessary and there are novel features in connection with the alloys themselves as well as with the methods of testing used for them. They seem, therefore, to possess many features of real interest outside the field of dentistry.

The viewpoint of the author in writing of these alloys is that of the practical producer rather than that of the physicist, thermoanalyst or the microscopist.

General Description of the Alloys

The alloys used in dentistry may contain a number of metals, as described later. In the great majority of cases, however, the largest percentage of the alloy by weight consists of precious metals. Among this group of precious metals would be included gold, silver, platinum, palladium and iridium. This high percentage of precious metal is dictated partly by the aesthetic demands of the dentist as well as the patient and partly by the fact that experience has shown alloys with high precious metal content to discolor and corrode in use in the mouth less than alloys with high base metal content. Other metals which may appear in the alloy in reasonable percentages are copper, zinc, tin and nickel. While all the elements mentioned above do not usually appear in a single alloy, the majority of them may and often do. The high strength alloys, particularly, often contain as many as five and six alloying elements.

The whole group of precious metal dental alloys may be divided roughly into the following four classes for the purpose of discussion:

1. Alloys to be used wrought or cast in which the requirement of high strength is not a prime factor
2. Alloys to be used in the cast condition where strength with accompanying necessary service ductility is of prime importance
3. Alloys to be used in the wrought condition, in which workability, strength, toughness and flexibility are of prime importance
4. Alloys whose melting point is of controlling importance, with other properties somewhat secondary, (that is solders).

The alloys of the first class are usually ternary, alloys of gold, silver and copper or possibly binary alloys. In such alloys the gold content usually ranges from 75 to 90 per cent of the whole by weight. The remaining portion of the alloy will be divided between the other two elements. This class of alloys is almost invariably yellow in color. The ultimate strength ranges from 25,000 to about 80,000 pounds per square inch, when tested (as described later) in the wrought condition. The proportional limit will range, roughly from 30 to 60 per cent of the ultimate strength, the higher percentage obtaining for the stronger alloys. Strengths and proportional limits of these alloys when used in the cast condition will usually be about 60 to 70 per cent of those of the same alloy in the wrought condition. Brinell hardness ranges from a minimum of about 35 to a maximum of about 170 for this class. Ductilities are usually good even if tested in the cast condition. Percentages of elongation as high as 25 per cent in 2 inches are obtained from some castings. This group of alloys react only slightly or not at all to heat treatment, therefore, alloys of this group do not offer very great possibilities of improvement in strength and hardness by heat treating. On the whole, this group of alloys is satisfactory for its purposes and is the one of those listed which is most nearly stable and the one on which the least amount of development work is being done at the present time.

Although it was previously stated that the first class of alloys usually contains only gold, silver and copper, there is some overlap. Moderately soft alloys will be found in the market containing considerable percentages of platinum and palladium. This is partly due to a demand for white alloys and partly to a widespread belief

in the intrinsic value of platinum metals which common usage has made to include platinum, palladium and iridium.

The second class of alloys have requirements paralleling very closely those of the third class. These are high strength coupled with necessary workability and service ductility. There are certain points of difference, however, dictated by the practical conditions of their use which require differences in their compositions. Both of these classes of alloys usually contain the three metals of the first class, gold, silver and copper. In addition to these, platinum or palladium, or both, will usually be found in greater or lesser percentages. To these elements is usually added small percentages of zinc, in the case of the second class alloys. Zinc does not usually appear in the alloys of the third class. The third class alloys, on the other hand, contain higher maximum percentages of platinum or palladium than do the second class alloys.

These differences in composition are necessitated by the fact that class-2 alloys are to be used in the cast condition. A reasonably low melting point is therefore essential, due to the limitations of available apparatus for heating the gold in casting. This limitation dictates lower percentages of platinum and palladium in class-2 alloys than in alloys of class-3, because these two elements invariably raise the melting point. The zinc content in class-2 alloys serves the purpose of reducing surface tension near the freezing point and improving the soundness of castings.

Class-2 alloys range in strength from the upper limit of class-1 alloys to ultimate strengths of about 110,000 to 115,000 pounds per square inch. These results are those of tension tests in the cast condition. Proportional limits will be at a maximum from 70 to 75 per cent of the ultimate strength. The strengths listed are for the heat treated condition (described later). Accompanying service ductilities are about one per cent in 2 inches as a minimum necessary requirement. Brinell hardness may range as high as 250 when tested after the alloy has been slowly cooled in the cast condition. These alloys are usually susceptible to hardening by proper heat treatment with an improvement in strength of from 60 to 80 per cent over that of the same alloy in the soft condition. There is a corresponding increase in hardness and a loss of ductility.

Class-3 alloys show ultimate strengths as high as 190,000 pounds per square inch as an approximate upper limit of strength when tested in the form of 19-gage wire. The accompanying ductility may

be as high as 3 to 4 per cent in an 8-inch length. The maximum Brinell hardness of these wires is from 290 to 300. The best of these wires will cold bend 180 degrees satisfactorily, two or three times around a mandrel producing an elongation in the outer fiber of about 25 per cent at each 90 degree bend.

In addition to the platinum-content alloys, described for the third class, there are a few of the ternary alloys of the first class which because of their high strength properly belong with the class-3 alloys. These few alloys are usually of rather low carat and have ultimate strengths as high as about 110,000 pounds per square inch, when accompanied by the necessary service ductility of, say, 2 to 3 per cent in 8 inches.

The fourth class alloys are used as solders in connection with golds of the first three classes. Generally lower melting points are required, therefore, than those of the alloys of the first three classes. This requirement becomes a controlling factor in the composition of the alloys of the fourth class. In general, the fourth class alloys are composed of the three elements, gold, silver and copper and the melting points are lowered by additions of necessary percentages of zinc or tin, or of both. These additions of zinc may reach a total of 10 per cent by weight in the lowest fusing of these alloys. The approximate accompanying ranges of melting point, (that is liquidus) is from a low of 1400 to about 1600 degrees Fahr. maximum. These fourth class alloys all react to heat treatment to a greater or lesser extent.

The low and medium karat solders react to heat treatment more markedly than the high karat solders. An 802 fine solder, i. e., 802 thousandths of gold, (about the highest karat solder used) does not react to heat treatment appreciably. Solders of fineness around 600 react most. Ultimate strengths hardened in the cast condition may attain 75,000 pounds per square inch with an accompanying ductility of about one per cent in a 2 inch length. The proportional limits are, roughly, 60 per cent of the ultimate strengths.

General Effects of Constituent Elements on the Properties of the Alloys

The number of alloys obtainable with the variations possible in constituent elements is enormous. Dr. O. E. Harder formerly of the University of Minnesota computed this number to be well over eight million by using 40 metals and assuming fairly large increments of

variation in the percentages of the elements which compose the alloy. The number of elements composing the alloys under discussion is not as great as this but critical increments in percentages of each element are much smaller than those used by Dr. Harder. The number of dental alloys actually on the market is large, although not nearly so great as that quoted above. The number of undeveloped possibilities is even larger.

It is quite obvious that a "cut and try" basis is the only one which could be used in dealing with a group of alloys whose complexity is as nearly infinite as that indicated. In general, this statement is true. It is not true, however, that this "cut and try" consists entirely of groping in the dark. There are certain perfectly definite general principles which are the result of both experience and research, by which development effort may be intelligently guided. In stating some of these principles below, the author wishes to emphasize the fact that while they apply generally to the commercially feasible alloys, they are approximate rules rather than exact facts and, consequently, all have their limitations and exceptions.

In constructing an alloy for dental purposes, the constructor is guided by certain definite requirements which are demanded in the finished product. These requirements are dictated by the use to which the alloy is to be put, feasibility of manipulation, and in some cases, by the prejudices of the user. In general, these are the same limitations which guide the preparation of any structural material. The important requirements which guide the manufacturer of a dental alloy might be partially listed as follows: melting point, resistance to discoloration or corrosion by the fluids of the mouth, ductility, strength, possibility of heat treatment, color and cost.

The first of the above requirements, the melting point, is limited for golds which are to be used in the cast condition, by temperatures obtainable with an ordinary gas torch using a forced air draft to a maximum temperature of from 1850 to 1900 degrees Fahr. (liquidus). Each of the alloying elements listed will have a traceable effect on the upper limit of melting range. In general, palladium, platinum, gold and silver tend to raise the melting point. That is if the percentage of any one of these elements were increased in an existing alloy, the resulting new alloy would have a higher melting point as a result of the addition, providing the melting point of the original alloy were below the melting point of the element added. The effects will be most marked for the different elements in the

order named above. It will be noted that their effect in raising the melting point is not in the order of the melting points of the elements listed. Palladium has a much lower melting point than platinum as an element but its effect in raising the melting point of the gold alloy is more rapid than that of platinum.

Copper, zinc and tin constitute another group of alloying elements, any one of which, if added to the alloy, as described above lowers the upper limit of the melting range. This is true of copper

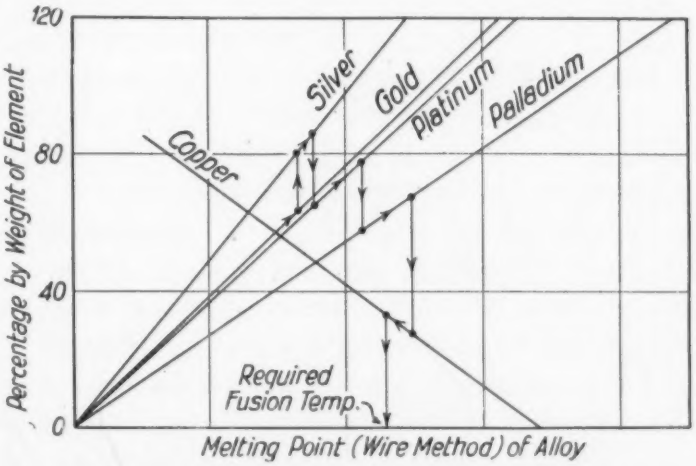

Fig. 1—Method of Showing the Quantitative Effect of Alloying Elements on Melting Point (Wire Method).

even though its melting point, as an element may be and usually is above the melting point of the alloy to which it is added. The melting points for zinc and tin are always below the melting points of the gold alloys to which they may be added.

Fig. 1 illustrates a method which the author has used to predict the effect of the various alloying elements on the fusion temperature (wire method) of the alloy. The arrows indicate the method of using the chart. The slope of each line is followed until a vertical distance has been attained equal to the content percentage by weight of that particular element. The fusion temperature is read vertically below after the effect of the last element has been traced. The slopes of the various lines indicate relatively the effects of the alloying elements on fusion temperature. No figures are given for temperature because such charts are limited to distinct groups of alloys and the publication of actual figures would be apt to be misinterpreted.

Resistance to discoloration and corrosion in the mouth is a matter which has not been much investigated. In general, the rare metals

which are also comparatively inert chemically, are credited with giving the alloy its resistance to corrosion in the mouth. These elements are platinum, gold and palladium, and, to a much less extent, silver. There is very little distinction in the mind of the average user of dental alloys between discoloration of the alloy in the mouth due to a deposit and corrosion of the alloy due to chemical action which might be measured in loss of weight, possibly. Tammann[1] has reported some results in connection with corrosion on the basis of loss of weight and is quoted by John Shell[2] that an alloy to be satisfactorily resistant to the mouth acids, should contain an atomic percentage of noble metal of 50 or more. Shell also states that in his opinion palladium should not be classed with gold and platinum in corrosion resistance. In actual practice the sum of atomic percentages of gold, platinum and palladium will range from 50 to 65. The sum of the percentages by weight of gold, platinum and palladium of the better alloys is usually 75 per cent or more of the total. When silver content is added, this total may reach as high as 90 per cent by weight. This statement does not hold true for gold solders, however. In the case of the solders, which rarely contain platinum or palladium, the gold and silver content very commonly is as low as 65 to 75 per cent, and the gold content runs as low as 45 per cent by weight.

Gold in common with most other metallic elements is very weak and ductile when pure. The addition of any of the alloying elements tends to strengthen it. These accretions of strength due to the various alloying elements may be divided into two classes, those obtainable by heat treatment and those obtainable without heat treatment. The former is dealt with under heat treatment. The best strength obtainable in alloys which are not subject to heat treatment and which contain usually very little copper, is a proportional limit in the neighborhood of 80,000 pounds per square inch, when tested in the form of 19-gage wrought wire. The corresponding ultimate strength will be in the neighborhood of 120,000 pounds per square inch. Such alloys may contain as much as 30 per cent platinum or palladium or both, as well as some silver. Platinum is the more effective strengthener.

Silver content is usually credited with benefiting the ductility of the alloy. Ductility on the other hand is entirely lost by contamina-

[1]G. Tammann, Text Book of Metallography, Chemical Catalog Co., New York City.

[2]Journal of American Dental Association, May, 1931.

tion of the alloy with mercury and lead. Very small quantities of either element render the alloy impossibly weak and brittle. Silver also serves as a controlling element over the rapidity and intensity of the reaction of the alloy to heat treatment. The possibilities of heat treatment are brought about largely through the agency of copper and gold, with platinum and palladium acting possibly as intensifiers but not essential to the process.

Color is affected by all of the alloying elements. The gold content lends its own color. Palladium is a very rapid whitener of the alloy. Under certain conditions, as little as 5 or 6 per cent of palladium may render the alloy white. Platinum whitens much less rapidly. An alloy whitened by platinum alone, might require as much as 20 per cent platinum and then not be a clear white. Silver whitens still less rapidly. Nickel is also a rapid and effective whitener. Copper lends a reddish cast.

Although the author knows of no law by which to justify the fact specific gravity of the alloy seems to be affected by each of the alloying elements, almost in proportion to its content by volume. The following formula gives a basis for computed specific gravities which checked 3 successive determinations each by a highly sensitive Jolly balance just as closely as these determinations checked each other for 5 wrought alloys of widely different composition. Such computations cannot be made for apparent specific gravity of alloys in the cast condition because of volume occupied by imperfections and discontinuities.

$$\text{Specific gravity} = \frac{100}{\frac{P_{au}}{S_{au}} + \frac{P_{ag}}{S_{ag}} + \frac{P_{cu}}{S_{cu}} + \frac{P_{pt}}{S_{pt}} + \text{etc.}}$$

P with its subscript denotes percentage by weight of the element in the alloy and S with its subscript the specific gravity of the element.

The compositions and specific gravities of the materials mentioned above follow:

Alloy	Composition Per Cent by Wt. Au	Ag	Cu	Pt	Pd	Ni	Sp. Gravity Jolly Balance[1]	Computed
1	63	11.5	13.5	10	2	...	15.78	15.4
2	65	13	17	1	2	2	14.39	14.5
3	62.5	10.5	24.4	..	..	2.6	13.70	13.75
4	66	13.5	14.5	4.5	1.5	...	15.87	15.1
5	47	36	....	..	17	...	13.97	13.8

[1]Each the average of 3 tests.

Heat Treatment

A great many of the dental alloys react to heat treatment. The improvement in strength resulting from heat treatment may amount to from 50 to 100 per cent of the strength of the alloy in its softest condition. This can be attained accompanied by sufficient ductility for structural service. There is, of course, a corresponding increase in hardness.

The reasons these alloys react to heat treatment have never been fully determined. Heat treating possibilities are usually attributed to the precipitation of certain compounds of gold and copper. Kurnakow[3] and others report the precipitation of the compound Cu_3Au at 371 degrees Cent. and less in binary alloys of gold and copper, for ranges of atomic percentages of gold between 25 and 35. They also report the compound CuAu for the same alloys between atomic percentages of 40 and 65. P. Y. Soldau[4] also reports the precipitation of the compound Au_3Zn in gold and zinc alloys of atomic percentages from 0 to 31 per cent zinc when cooled below 450 degrees Cent. and AuZn in alloys containing atomic percentages of zinc from 38 to 51. Just what part each of these compounds determined for the binary alloys plays in the heat treatment of the more complicated alloys of commercial use is not determined. There are certain facts, however, in connection with the heat treatment of these alloys which are known from practical experience and which seem pertinent to the case:

1. No commercial alloys on the market which do not contain copper, react to heat treatment sufficiently to give enough return in structural benefit to reward the efforts of heat treating.
2. Not all alloys containing copper react to heat treatment sufficiently to warrant the effort commercially.
3. Certain other alloying elements, such as silver and platinum, while not essential to the heat treating effect, do seem to exert an influence on the results.

An exception to the first statement might be noted in the case of some of the high nickel alloys. These, however, are not used to a great extent in high grade dental practice. In general, the percentage of copper required to cause an alloy to heat treat sufficiently to make the effort worth while in structural benefit obtained, ranges from 8 to about 17 per cent by weight, depending upon the alloy.

[3] *Journal*, Institute of Metals, 1916, Vol. 1.

[4] *Ann. Inst. Phys. Chim.*, Vol. 2, 487-8 (1924). *Chemical Abstracts*, Vol. 21, (2654) (1927).

Ternary alloys of gold, silver and copper will usually require somewhat more copper to obtain the full heat treating effect than will the more complicated alloys which contain platinum and palladium. Some alloys contain more than 17 per cent copper by weight but it has been the author's experience that this added copper produces no benefit in the heat treating of the alloys and may be detrimental to their strength. When the percentages of gold and copper are expressed on an atomic basis their relationship to heat treatment becomes more

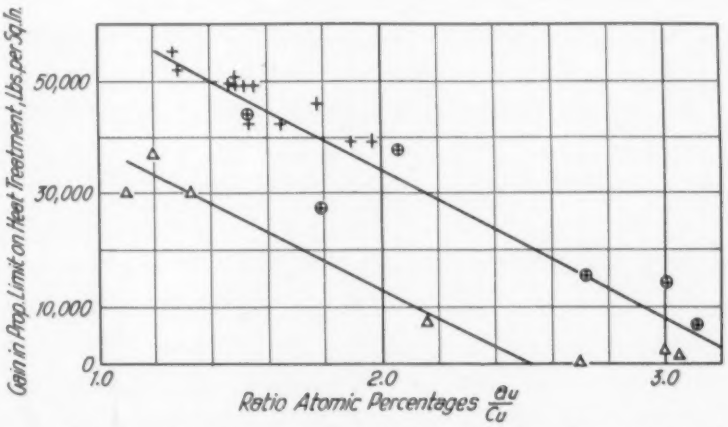

Fig. 1A—Showing the Relationship Between Improvement in Proportional Limit on Heat Treatment and the Ratios of the Atomic Percentages of Gold and Copper in the Alloy.

\+ Wrought alloys containing platinum.
* Alloys in cast condition containing platinum.
Δ Alloys containing no platinum.

readily traceable. Fig. 1A illustrates this statement. It will be noted that there is a very definite relationship between improvement in proportional limit and the atomic ratios of Au-Cu. The influence of platinum on heat treatment is also shown by the fact that the average trend for the plantinized golds lies considerably above that for the non-platinized golds though the two are parallel.

Description of Heat Treatment

Heat treating of dental alloys in the United States has been very largely influenced by the work of the National Bureau of Standards[5]. This is especially true with regard to the temperature used for quenching in softening and for slow cooling in hardening.

The alloy may be heat treated either for softening or for hardening. The heat treatment for softening consists in heating to a

[5]R. L. Coleman, Research Paper of the U. S. Bureau of Standards No. 32.

uniform red heat (1300 degrees Fahr.) and plunging quickly into a cooling bath. In some cases a double quench, that is, a second heating and quenching, will produce increased softness.

The time during which the alloy is held at 1300 degrees Fahr. before quenching may also contribute to the result obtained. Generally the longer it is held at this temperature before the plunging the softer will the metal be. This result has generally been attributed to grain growth in the case of wrought alloys but it is doubtful whether the phenomenon can be fully explained so.

The author has test results on two alloys in both the wrought and cast conditions held at 1300 degrees Fahr. for various lengths of time up to 30 minutes, before plunging, in each of which the softening effect due to holding was fully as great for the cast as for the wrought samples. Since grain growth in cast metals is not usually conceded this would seem to indicate some other explanation for the additional softening due to holding.

The alloy may or may not react to the temperature of the quenching bath. Below is shown the Brinell hardness of three different wrought alloys quenched in ice water, water of room temperature, and boiling water:

	Compositions					Brinell Hardness of Alloy Quenched in Water at Temp. Shown—		
Alloy	Au.	Ag.	Cu.	Pt.	Pd.	3 Degrees Cent.	29 Deg. Cent.	100 Deg. Cent.
A	63	11.5	13.5	10	2	173	188	204
B	59	8	13	17.5	2.5	207	205	213
C	66.75	17	16.25	..	...	130	136	129

It will be noted that only in the case of alloy A is there any noticeable effect on the Brinell hardness, due to the different temperatures of the cooling medium. Water is commonly used as a cooling medium. Other media used are alcohol, oil and a hot solution of sulphuric acid.

The softening effect of quenching may increase with the thermal conductivity of the cooling medium. Alloy A above showed about 12 per cent less Brinell hardness when quenched in water at room temperature than it did quenched in alcohol or oil, which have only about one-third the conductivity of water. This was not, however, true for alloys B and C. These alloys were tested in the wrought condition.

The heat treatment of the alloy for hardening consists in the preliminary heat treatment for softening just described, a subsequent reheating to 840 degrees Fahr., and cooling the alloy from 840 to 480

degrees Fahr. in a specified time as recommended by the Bureau of Standards. After the cooling period is completed the alloy is quenched in a cooling medium just as it was after the heat treatment for softening. The Bureau of Standards recommends thirty minutes for this cooling out period. This period, however, is so long that in addition to being somewhat time consuming it leaves otherwise perfectly serviceable alloys too brittle. A much shorter period will often give practically as good strength with better ductility. As a matter of fact, by far the greater proportion of the strengthening effect of slow cooling is produced in the early stage of the cooling period. For instance, alloy B above attains fully 50 per cent of its increase in strength in the first five minutes of a thirty minute cooling period.

During heat treatment, the alloy blackens from oxidization due to its copper content. Quenching in either hot acid or alum will remove this oxide. Alcohol will also leave the surface comparatively bright but with a reddish deposit. Water will leave the surface black.

The method of handling alloys in reheating to 840 degrees Fahr. after quenching is important to the result of heat treatment. If the alloy is put in a furnace and gradually brought to a temperature of 840 degrees Fahr. over a comparatively long period of time, this soaking during the reheating may have the same effect as the cooling period in producing hardening. Publications of the Bureau of Standards are silent on this point. The author's practice of heat treating has been to bring the furnace to a constant temperature of 840 degrees Fahr., then place the specimen to be heat treated in the furnace and allow it to remain a minute and a half for 19-gage wire and two minutes for 0.08-inch cast specimens, before starting the cooling period. It is felt that these times are ample to allow the specimen to absorb the temperature of the furnace and they are reasonably in line with the recommendations of the A. S. T. M. for ferrous metals.[6]

The Bureau of Standards in their Research Paper No. 32 makes the following statement in regard to heat treatment:—"It was also found that the time required to produce a given degree of hardening was practically the same whether the alloy was held at a constant temperature or allowed to cool slowly. For example, cooling the

[6]American Society for Testing Materials Specification A-35—24.

alloy from 840 to 480 degrees Fahr. in thirty minutes produced practically the same effect as heating at 840 degrees Fahr. for thirty minutes. These findings were verified by tests of the various mechanical properties." It is true that an effect of increase in strength and hardness may be produced in most alloys by prolonged heating at a constant temperature, somewhat similar to that which is produced by the slow cooling described above. It is the author's experience, however, that this effect is never as great for a given soaking period as that produced by a slow cooling for the same period.

In some alloys, soaking at 840 degrees Fahr. produces very little or no traceable hardening effect. For instance, alloy A noted above, when soaked at a constant temperature of 840 degrees Fahr. for five minutes, showed a proportional limit of 115,000 pounds per square inch. When soaked for 10, 15, 20 and 30 minutes respectively, its proportional limit dropped to 108,000, 102,000, 92,000 and 85,000 pounds per square inch. In all cases, the ductilities were comparatively low. Alloy A normally has a proportional limit of 125,000 pounds per square inch when slow cooled for five or ten minutes. Alloy B above showed a proportional limit very nearly constant around 120,000 pounds per square inch when soaked at a temperature of 840 degrees Fahr. for 5, 10, 15, 20 and 30 minutes, while its proportional limit on slow cooling for 15 to 20 minutes is 135,000 pounds per square inch. Another alloy consisting of gold—65 per cent, silver—13 per cent, copper—17 per cent, platinum—1 per cent, palladium—2 per cent, and nickel—2 per cent, showed no effect of heat treatment when soaked at 840 degrees Fahr. although it exhibited marked effects when slowly cooled from 840 to 480 degrees Fahr. It reacted markedly, however, to soaking at a constant temperature of 600 degrees Fahr. Alloy A, above, when soaked at 600 degrees Fahr. for five minutes showed a proportional limit of 86,000 pounds per square inch and when soaked at the same temperature for thirty minutes showed a proportional limit of 100,000 pounds per square inch. Thus when soaked at the high temperature, the proportional limit of alloy A dropped with increase in time while at the lower temperature, it rose as time of soaking increased.

It appears that possibly there is a most favorable constant temperature at which each of these alloys could be soaked and heat treated satisfactorily. The variable temperature cooling period seems however to give on the whole better results due to the fact that there

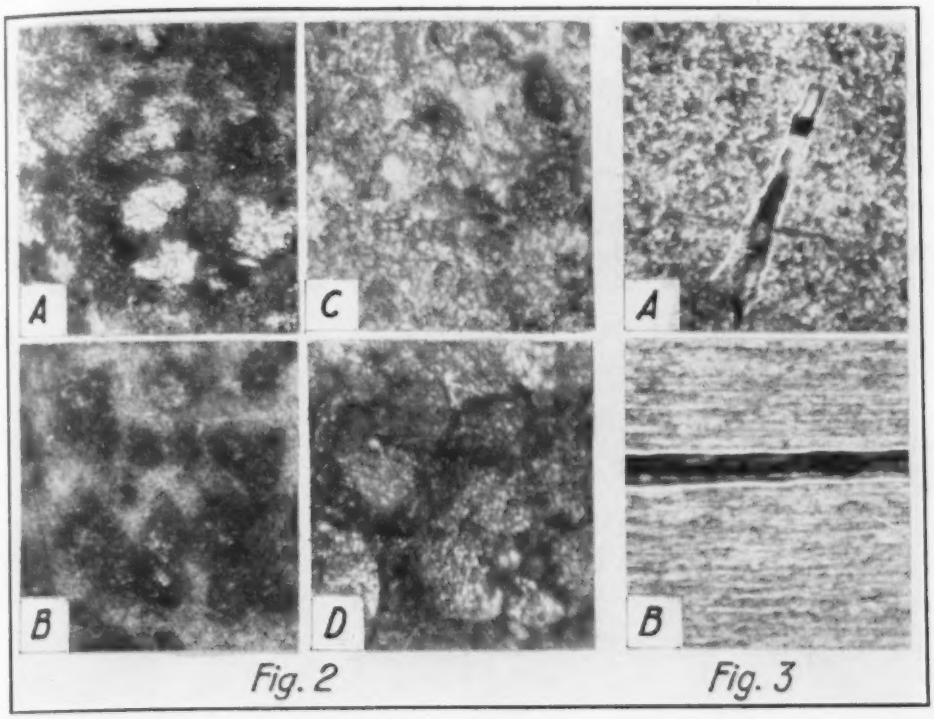

Fig. 2 Fig. 3

Fig. 2—Photomicrographs of a Gold Alloy in the Cast Condition Showing Changes in Structure After Heat Treatment. (A and C) Quenched in Water from 1300 Degrees Fahr. (B and D) Slowly Cooled from 840 to 480 Degrees Fahr., in 20 Minutes. (A and B) Etched with Iodine, (C and D) Etched with Aqua Regia. × 500.

Fig. 3—Photomicrograph of a Piece of Wrought Wire Showing a Platinum Segregation. (A) Cross Section. (B) Longitudinal Section. × 100.

is an increased likelihood that somewhere during the cooling period the most favorable temperature is attained for the particular alloy being heat treated. The working out of the exact heat treatment best suited to each alloy might have some slight advantages but because of the confusion resulting from the number of heat treatments necessary the variable temperature cooling period is most satisfactory at present.

Very little work has been done with a view to determining the permanency of the properties attained through heat treatment over a period of time. The author has test results on six alloys in the form of wrought wires each tested at periods of time after slow cooling of 4, 28, 52 and 120 hours and again at two months. None of the six alloys showed much change in ultimate strength for periods within the first 120 hours. Four of the alloys held a constant ultimate strength over a period of two months. One of the alloys showed a 35 per cent increase in ultimate strength at the end of two months.

The other showed a 22 per cent decrease in strength at the end of the two-month period. These figures are based on 3 or more tests of each alloy at each age.

The compositions of the alloys showing variation of strength with age are given below.

	Compositions				
	Au	Ag	Cu	Pt	Pd
Alloy Showing Strength Decrease	63	11.5	13.5	10	2
Alloy Showing Strength Increase	62.5	10.5	24.4	..	..

Some investigators of precious metal alloys have reported effects of heat treatment to be traceable by the microscope. The micrographs shown in Fig. 2 of a piece of cast gold in both the quenched and the slow cooled conditions show these differences of structure. In spite of the fact that these differences exist, the microscope at the present time has no definite place in interpreting the effects of heat treatment because of the lack of a recognized method of interpretation, such as exists for instance in connection with steels.

About the only definite usefulness which is made of the microscope at the present time is in examining the alloys for relative grain size and in detecting porosity, segregations, etc. Fig. 3 shows one of such segregations consisting, in this case, of platinum metals, which was proved by the fact that the surrounding alloy melted away when wire was held in the open gas flame, leaving the segregation of high fusing metal intact. Fig. 3-A shows the segregation in cross section and B in longitudinal section where it has been drawn into a thread due to the drawing of the wire through the die. Platinum segregations appear dove gray in the microscope, little affected by etching reagents. It is to be hoped that means will be developed for making microscopic interpretations of heat treatment effects better understood.

Most of the gold alloys in common with many of the brasses reach a stage of extreme weakness and brittleness at temperatures between red heat and room temperature. Some of the alloys may be bent and shaped at a bright red heat but none can be shaped at elevated temperatures below a red heat.

Methods of Testing

There are several points in connection with the methods of testing these alloys which are of general interest. These methods have been rather fully standardized by the Gold Group of the American

Dental Trade Association. They are somewhat unique in that they deal with very small sections and, consequently, embody features which are different from those ordinarily used in connection with the larger sections tested for steels and brasses. These methods have also been influenced by the work of the Bureau of Standards, previously quoted.

For wrought wires, the test specimen is an 0.036-inch (19-gage) wire, 12 inches long with an 8-inch gage length; for rolled plates it is a flat strip 0.007 inch thick by 0.025 inch wide with an 8-inch gage

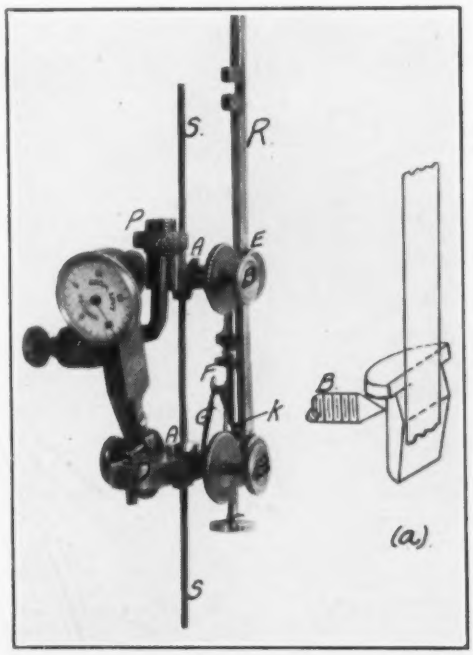

Fig. 4—An Averaging Extensometer Meeting the Requirements of the Standards of the Gold Group of the A. D. T. A. for Testing Gold Alloys.

length; for cast metals a cast specimen 0.08 inch in diameter by 5 inches long tested in tension with a 2-inch gage length. An averaging strain gage is required except for the 0.036-inch wrought wires. The required accuracy is 0.0005 inch for the 8-inch gage length and 0.00025 inch for a 2-inch gage length. The accuracy required for the testing machine is $\pm$ 0.5 pound.

The Baby Brinell hardness test is used. This has been adapted from the test developed for cartridge brass during the war and reported in A. S. T. M. Proceedings for 1919[7]. This test consists of

[7]Development of Hardness Tests on Thin Brass Sheet by S. L. Goodale and R. M. Banks.

forcing a one-sixteenth inch steel ball under a 28-pound load, into the surface of the test specimen. The hardness is expressed in terms of load in kilograms, divided by the area of the spherical indentation in square millimeters. The area of the indentation is based on measurements of the diameter of the impression, made with a filar eye piece or a projecting microscope magnifying about 150 diameters. These Baby Brinnell hardness results give substantially the same hardnesses as do regular Brinell tests using a 10-millimeter ball and a 500-kilogram load. The author has a dozen or more parallel test results on different alloys with hardnesses ranging from 80 to 250 Brinell made with the two different pieces of apparatus. The differences between the results of the Baby Brinell test and the regular Brinell test are small, being no greater than occur between different impressions by the regular Brinell apparatus.

The adopted standards of the A. D. T. A. Gold Group treat the temperature at which the alloys melt from two different standpoints. Their attitude toward alloys which are to be used in the wrought condition is that the user, since he is not going to melt the alloy, is only interested in the maximum temperature at which the alloy has appreciable strength and at which it might be safe to heat it in his manipulation and that he is not interested in the melting point, that is the liquidus. For alloys which are to be cast by the user or melted as in the case of solders, the standards call for the complete melting range, solidus and liquidus.

In the case of the wrought alloys the temperature reported is called "fusion temperature." It is the temperature at which an 0.0285-inch wrought wire of the alloy, one-sixteenth inch long, which has been welded between the extremities of the leads of a platinum-rhodium thermocouple will break when subjected to a cross bending load of 3 ounces avoirdupois. This test was developed at the Bureau of Standards. The fusion temperature so determined usually lies within the melting range as determined below for cast alloys. It is often about halfway between the solidus and liquidus but from the experience of the author usually tends to lie somewhat nearer the solidus. In the case of some of the solders, however, it is entirely below the melting range. The fusion temperature for most alloys checks for the successive tests quite closely. In a few cases, however, as, for instance, pure gold, there is more variation between successive tests.

The melting range which is reported for all cast golds and

solders has for its upper limit the solidus and for its lower limit, the liquidus, as determined from the inverse rate cooling curve. An accuracy of result of plus or minus 18 degrees Fahr. is required. The sample used in the determination weighs 100 grams or more.

Various extensometers are used to measure elongation of test specimens. Fig. 4 shows one the author has developed to meet the requirements for testing each of the various test specimens listed above. This extensometer is patterned somewhat after the well-

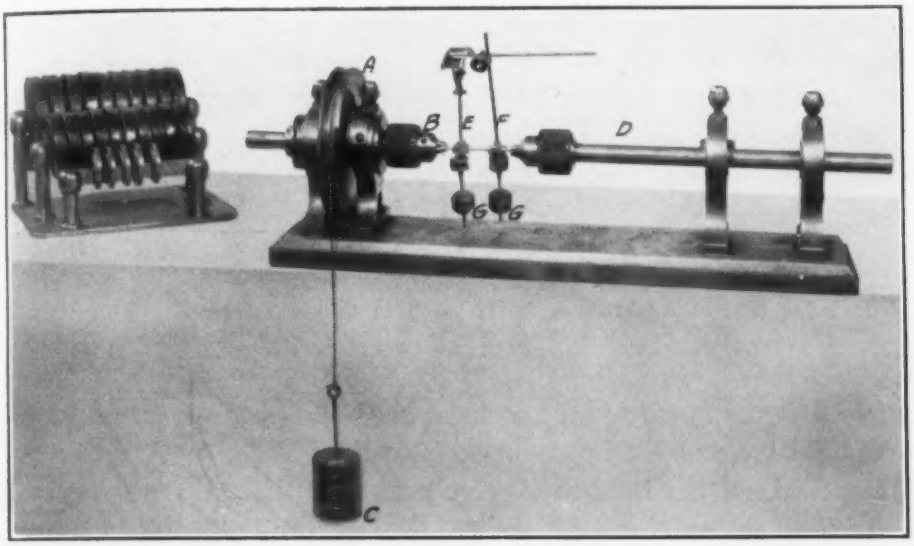

Fig. 5—Apparatus Developed for Testing 0.036-Inch Wrought Wires in Torsion.

known Ewing extensometer. The specimen S-S which may be either a wrought wire, an 0.08-inch cast specimen or an 0.007-inch by 0.25-inch band is held in the heads of the extensometer by means of the set screws B. These screws bear against the chucks (A) a detail of one of which is shown in Fig. 4 (a). These chucks, one pair in each head, bear against the specimen at the peak of the tapered portion directly opposite the point of set screw B, and hold the specimen by friction without scarring it. The chuck shown in Fig. 4 (a) is for the band specimens. Those for the wires have a tapered groove.

The upper head of the extensometer EA holds a fixed angle with respect to the test specimen due to the fact that joint at E rotates only in a plane at right angles to Bar EA. Bar EF is pivoted to adjusting screw C at K, and the lower head is held firmly against this pivot by means of the taut rubber band G.

As the specimen elongates point D moves vertically approxi-

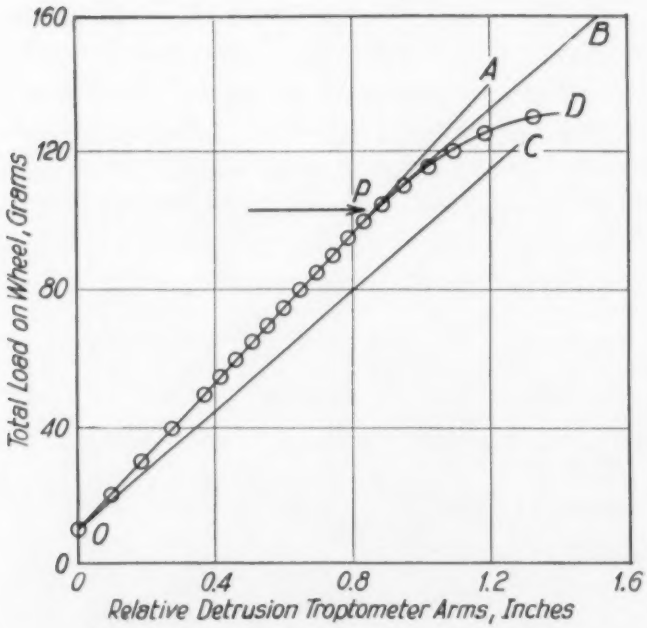

Fig. 6—Curve of Torsion Test Obtained from Apparatus of Fig. 5, Showing Method of Locating the Modified Johnson's Apparent Elastic Limit.

mately twice as much as the specimen at B elongates. This multiplied movement is recorded by means of the Last Word Gauge, fastened rigidly to the upper head at P. An Ames dial is sufficiently accurate to use with the specimens of 8-inch gage length, and is often substituted for the Last Word Gauge in testing these specimens, because of its greater range. The gage is applied to the specimen by means of an auxiliary reference bar R, which is constructed for a 2-, 4-, or an 8-inch gage length, and is removed after the instrument is adjusted to the test specimen.

This is an averaging gage which meets all the requirements of the standard methods for testing these alloys. The upper head is light enough that the error made in failure to correct stresses in the test specimen for its weight is small.

The author has also developed a piece of apparatus for testing these small wires, or the 0.08-inch cast specimens in torsion. This test is not included in the standard methods adopted by the members of the Gold Group. This piece of apparatus is shown in Fig. 5 with an 0.08-inch specimen inserted. It consists of a grooved pulley, mounted in ball bearings, carrying the smallest size Jacob's drill chuck on the end of the shaft, shown at (B). This pulley is wrapped with fish line at the end of which is fastened scale pan C, or a

basket when testing wrought wires. The weight of this pan or basket is just right to overcome the static friction of the shaft of the wheel in the ball bearings. Opposite to the movable chuck is fastened a fixed chuck on the end of the shaft D, which is free to slide endwise but not to rotate. A piece of 19-gage wire is clamped between these chucks with about an inch clearance. The troptometer arms E and F are fastened to the wire about three-quarters of an inch apart. One of these arms carries a flexible steel scale bent into a circle of about 2.85-inch radius, the other carries a magnifying glass focused on the divisions of the steel scale. The arm E is adjusted so that the distance from the center of the wire to the scale is the right amount to make a detrusion of 0.01-inch equivalent to 0.2 degrees rotation. The troptometer arms are each counter-balanced (G) so that their weight will not affect the torque on the test specimen. Loads are applied usually by adding 5-gram weights to the basket C. After the weights are added, the frame of the apparatus is tapped gently with a piece of wood to overcome the inertia effect of the grooved wheel. As soon as movement ceases, the tapping is stopped and the reading of torque and detrusion recorded. This apparatus gives smooth consistent curves of which Fig. 6 is an example.

In general the proportional limit in shear of most of the gold alloys will average a little more than half of the proportional limit in tension. The modulus of elasticity in shear is usually a little more than a third of the modulus of the same material in tension. The modulus of elasticity of dental alloys in tension ranges from 14,000,000 to 18,000,000 for wrought alloys. The computed value of Poisson's ratio, or the factor of lateral deformation is consequently from 0.3 to 0.4 which is a little more than for steels.

Fig. 6 illustrates the standard method of determining a modified value of the well-known Johnson's apparent elastic limit which is peculiar to these methods of test and has a great deal to recommend it. A line PB is drawn tangent to the average curve OPD, which makes 25 per cent greater slope with the stress or load axis than does the straight part of the curve OP. Instead, however, of using the point of tangency with the curve as the value of the apparent elastic limit as is done in determining the Johnson apparent elastic limit, the point of intersection P of this tangent line with the original straight part of the curve OA is taken as the apparent elastic limit. This practice has the same advantage of being perfectly definite which

the Johnson method has, and the added advantage that it locates the apparent elastic limit much closer to the ordinary proportional limit value than the Johnson method. As a matter of fact, with some of the very brittle cast materials which are tested, the use of the ordinary method of determining Johnson's apparent elastic limit always locates this value at or very near rupture.

A surprising amount of research in connection with precious metal alloys is being carried out at the present time in view of the relative amount of business available to the precious metal industry as compared to other metal industries. The American Dental Association has two Research Fellows at the Bureau of Standards in Washington devoting full time to research in dental materials. Most of the leading manufacturers of dental alloys have research equipment and men actively engaged on their problems. A fine spirit of cooperation exists between the various agencies engaged in research, resulting in the standard methods of test previously mentioned and the beginnings of the writing of specifications for certain classes of alloys recently instituted at the Bureau of Standards.

Most of the problems attacked so far in this country have been of a more or less practical nature, research from a purely scientific standpoint having been somewhat secondary. Some fundamental research has been done, however, mostly in Europe. A great deal more remains to be done, particularly research of a fundamental nature, in order to really acquaint ourselves with these very complicated precious metal alloys.

The work which the author has done with the precious metal alloys has been in connection with the J. F. Jelenko Company of New York City.

Below is appended a partial Bibliography for a portion of which the author is indebted to W. S. Crowell.

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DISCUSSION

Written Discussion: By Walter S. Crowell, technical assistant to vice-president, S. S. White Dental Mfg. Co., Philadelphia.

Mr. Brumfield's paper surveys the precious metal alloys used in dentistry and briefly describes their composition, physical properties and response to heat treatment. His description of the role of the various alloying elements in producing precipitation hardening might be said to agree with the data obtained from tests of the commercially available alloys. Before accepting it

without qualification, however, the author's statements at the close of the paper, concerning research on precious metal alloys, must be carefully noted.

As he points out, most American workers have had practical problems to solve, with little time for pure research. This seems to have led to the development of alloys which respond to certain stereotyped heat treatments and the assumption that those which do not are, under all conditions, free from precipitation hardening.

The temperatures and compositions limiting the age hardening of gold-copper are given by Kurnakow, et al. The effect of the addition of silver on these limits is shown by the work of Sterner-Rainer. The age hardening of platinum-copper and palladium-copper is indicated by Nowack and others. A study of these references gives valuable data on limiting and optimum copper content.

The strengthening effect of additions of platinum metals to gold-silver-copper alloys is mentioned by the author. This is a phenomena of great practical importance. The high strength alloys of gold-silver-copper occur below 50 atom per cent gold and are undoubtedly deficient in corrosion-resistance for dental purposes. Using both gold and platinum metals, alloys of high strength and response to heat treatment can be produced at precious metal levels sufficiently high to insure adequate corrosion-resistance. Where high strength and corrosion-resistance are required the platinum metals play a part second only to copper.

Written Discussion: By John S. Shell, assistant professor of chemistry and metallurgy, University of California, College of Dentistry, San Francisco, California.

The interest recently shown by the dental profession in developing and perfecting the materials which they use, is well evinced in this excellent paper on precious metal alloys. Such reports are valuable not only because of the data presented, but also as a means of breaking down the almost insurmountable wall of secrecy that so long surrounded the production of gold alloys. Secrecy of procedure and alloy composition are only recently being discarded as advertising copy by dental manufacturers and are being replaced by information regarding the physical properties of each alloy produced. This has reacted favorably toward the development of more advanced technical procedures on the part of the dental profession.

As stated by Mr. Brumfield, the commercial application of high strength precious metal alloys is limited almost entirely to the dental field. Considering the high strength of such alloys combined in many cases with absolute chemical resistance to such powerful reagents as concentrated nitric and sulphuric acids, it is surprising that they have not found many other commercial uses. As has been stated, cast alloys are readily prepared with an ultimate strength of 110,000 pounds per square inch and wrought alloys can be obtained with ultimate strength of 190,000 pounds per square inch. With physical properties as indicated in the paper it would seem that the alloys might find many uses in structures of small sizes requiring high strength and freedom from corrosion.

The differentiation between discoloration due to foreign deposits and that due to actual chemical attack cannot be over-emphasized. To these causes for

discoloration might also be added the effect of electrolytic decomposition resulting from the presence of two or more types of metal restorations in the same oral cavity. Many mouths contain combinations such as silver-tin amalgams, pure gold foils, and alloys containing a gold content as low as 16 karat. Very little investigation has been reported relative to any of these factors. Tammann's work seems to give the only available scientific basis for determining the probability of direct chemical attack from the fluids of the mouth. According to Sterner-Rainer only gold, platinum and iridium are absolutely free from acid-corrosion. He omits palladium from this list due to its action with hydrochloric acid and silver is not considered corrosion-free in any sense as it reacts on chlorides and sulphides.

According to Grigoriev the alloys of gold and platinum which do not contain too small a percentage of either metal decompose into an eutectic mixture after partially solidifying as a solid solution. This may help to explain the effect of platinum during the heat treatment of alloys containing this metal. Nowack finds it possible to produce age hardening in the binary combinations gold-platinum, palladium-copper, and platinum-copper, as well as gold-copper. The cause of the marked effect of silver in increasing the rate at which the hardening proceeds is not clear.

In slowly solidified alloys of gold and copper containing equal atomic percentages, long heat treatments (1 to 24 hours) are easily demonstrable by microscopic examination. The Widmanstätten structure usually develops in the heat treated specimens as opposed to the solid solution structure in the quenched alloys. In the more complicated alloys little or no change in microscopic structure is observed during short heat treatments (5 to 30 minutes). Structural changes resulting from such heat treatments in these alloys are more probably due to a diffusion of the segregated alloy resulting from liquation, tending to produce a homogeneous structure. These changes may affect the physical properties, but there is no definite evidence to indicate that the observed phenomena parallel the structural modifications observed by the microscope.

Written Discussion: By N. O. Taylor and G. C. Paffenbarger, research associates of the American Dental Association, and Wilmer Souder and W. T. Sweeney, staff members, dental laboratory, U. S. Bureau of Standards, Washington, D. C.

The author, Professor Brumfield, has reported some interesting phenomena which have only recently become general information among many of the users of these alloys.

Our primary criticism of the report is the apparent reluctance to give formulas of alloys[1] and the qualitative type of data mentioned for these practically hidden alloys. These two evasions rob the report of much of its scientific interest. The abstract appearing under the title of the paper states, "There are a number of precious metal alloys which embody good possibilities for structural service . . . ." Doubtless many members of the society would

[1]**Editor's Note**—Subsequent to the preparation of this paper in preprint form for distribution prior to the convention the author, Professor Brumfield, has made numerous additions to his paper especially in regard to the compositions of the alloys discussed. In view of these additions some of the discussion of this paper becomes invalid.

welcome such alloys for use in special design or service; but not one alloy is completely described and the only direct access to an alloy formula for such special service (so far as this report is concerned) would be by reference to Research Paper of the Bureau of Standards No. 32 by R. L. Coleman, which the author lists in his references.

The absence of numerical values on Fig. 1, formulas for Alloys A, B, and C, and the six alloys mentioned on page 347 makes it impossible for research workers in this field to derive any important benefits from the report.

In the discussion of color, page 341, a word of caution should be given on the tendency of silver to turn these alloys to a greenish color and on the possibility of nickel seriously reducing precentage elongation in certain alloys. Manufacturers supplying dental alloys for use by government departments have come to grief by reason of these defects.

Specific gravity is not regarded as of special interest in our present research with these alloys and we are not prepared to discuss the formula or conclusion drawn. Likewise the torsion equipment shown in Fig. 6 is not used in our work since it is thought the combined properties which it gives are secured separately in the regular elastic tests reported in Research Paper No. 32 mentioned previously. It is also suggested that those interested in securing most accurate values for percentage elongation see Fig. 34 in Research Paper No. 32 for a double dial type of extensometer. This will be found more satisfactory for the greater elongations than the equipment pictured in Fig. 5 which might become less accurate by reason of the lack of parallelism between the extensometer, specimen and pivoted bar.

The section on heat treating is not clear to any of the discussers and for several reasons should be rewritten. Reference to the Bureau's research should be elaborated to show how and why the ranges of temperature and time of heating were selected. Perhaps a better résumé could be as follows: The Bureau of Standards has given data on various periods and temperatures for heat treatment and has selected as a safe cooling range 450 to 250 degrees Cent. and time interval of thirty minutes.

This interval of 30 minutes is doubtless longer than is necessary for some alloys and undoubtedly does render certain alloys extremely brittle, as explained on page 880—Research Paper No. 32. There are, however, numerous alloys which respond nicely to this treatment and it is not so critical as the 5 or 10-minute intervals sometimes recommended. To illustrate, an error of 5 minutes overtime on a 10-minute cool of alloy A, page 345, gives a change of 6000 pounds per square inch in proportional limit whereas the change for an overtime cooling of 35 minutes instead of 30 minutes would produce probably (no curve available) less than half the change. This is further emphasized by alloy B, page 344, where 50 per cent of the enhanced value for heat treatment is developed in 5 minutes; the remaining 50 per cent being developed during the next 25 minutes. From these examples we see that small errors of time intervals may prove very serious on the critical or short time range heat responding alloys unless each dentist equips his laboratory with an automatic time switch, or watches the time closely; whereas with the longer period he is not tied to such exacting time intervals. It would be difficult for users of dental alloys to meet all possible combinations of time and temperature from

5 minutes to 30 minutes and from 600 to 200 degrees Cent. which might be recommended by the various manufacturers of this commodity. For the greater safety to the dentist the above intervals of time and temperature are selected for use until such time as agreement upon better intervals could be secured.

Written Discussion: By R. B. Elliott, assistant director, research laboratories, Williams Gold Refining Co., Buffalo.

Those associated with precious metal research are indebted to Mr. Brumfield for his compilations and opinions on the behavior of precious metal alloys.

Work conducted in our laboratory[2] in collaboration with Dr. Walter H. Ellis, orthodontist, has demonstrated that no perceptible change occurs in 20 per cent platinum spring wires, subjected to air-cooling from 1300 degrees Fahr., after two, three and eight months' exposure in the mouth. This was shown primarily by metallographic means, secondly by physical tests. In the event that the properties changed, it could be traced to local cold work caused by the practical operation of the appliance. To theorize, heat treatment is an endothermic process and therefore should be unstable at room temperature, but the return to normalcy is so slow as to be imperceptible, and the alloy remains in a metastable state. Cold work, being a form of energy, encourages this forward transformation.

Mr. Brumfield has neglected to explain the method of initial alloying in the case of the platinum segregation in the wrought wire he examined. At the time of the inception of complex platinum alloys into dentistry we were using gas furnaces for alloying operations, and this segregation is typical of the difficulties we also encountered until we adopted the method of high frequency induction. Since that time we have entirely obviated the trouble. In addition to being able to attain temperatures in the neighborhood of 3400 degrees Cent., well above the melting point of any of the platinum group metals, there is the advantage of an electromagnetic stirring of the melted metal, i. e., the pinch effect, both together insuring perfect homogeneity in the resulting alloy. Performing the melting operation in hydrogen, nitrogen, or even in vacuo is optional. So gratifying have our results been in this phase of precious metal melting that we are now endeavoring to extend the principle to the actual dental casting operation.

Dental alloys in common use have melting points between 800 and 1400 degrees Cent. When these alloys are in the molten state they must be forced into a mold and every possible precaution taken to prevent blow holes or other imperfections in the casting. With the present open flame method of melting, good castings are difficult to secure and the work requires great skill.

Our scheme of adapting high frequency melting to this operation is quite simple. The wax pattern is invested in very dense artificial stone poured into a split flask. Upon the setting of the stone, the flask is removed and a crucible is formed in the stone directly above the wax sprue lead. Heating to 650 degrees Cent. burns out the wax and dehydrates the mold. The invested form, with the correct amount of gold alloy in the crucible, is placed beneath a ground glass bell jar and the latter is evacuated to less than 6 millimeters

[2] R. V. Williams, "Orthodontic Alloys," *The International Journal of Orthodontia, Oral Surgery and Radiography*, Vol. XI, No. 1, January, 1925.

pressure, indicated by a manometer. High frequency energy, radiated from a water-cooled coil outside the bell jar, then melts the metal over the evacuated chamber. The releasing of the vacuum within the bell jar forces the molten alloy into the evacuated form. Upon cutting out the high frequency radiation the alloy solidifies in situ.

The source of high frequency current is either a vacuum tube[3] or a spark gap[4] converter, the former having a frequency of about one and one-half million and the latter one of ca. 40,000. For melting very small amounts of metal for single tooth inlays, permitting the use of a very small inductor coil the higher frequency is desirable; for fusing larger amounts of metal for, let us say, a full denture the lower frequency is preferable, a larger inductor coil being used.

Test rods have been cast of a 6 per cent platinum-gold alloy by the above method and found to give the following physical properties:

Condition	Proportional Limit Lbs. per Square Inch	Ult. Tens. Strength Lbs. per Square Inch	% Elongation
Quenched	60,300	74,300	9
Oven-cooled	118,000	123,000	1

These show marked superiority over the properties of rods cast by oxy-gas and air pressure:

Condition	Proportional Limit Lbs. per Square Inch	Ult. Tens. Strength Lbs. per Square Inch	% Elongation
Quenched	54,200	68,000	6
Oven-cooled	81,500	103,000	1

Dental cases can consequently be cast much thinner and lighter and still retain their necessary strength.

Written Discussion: By R. L. Coleman, director department of metallurgy, J. M. Ney Company, Hartford.

The paper by Mr. Brumfield presents material that should prove interesting and informative to those who are interested in metals but who have not had occasion to keep in touch with recent developments in the precious metal alloy field. Little new or definite data are presented, but the paper should serve to bring some of the rather remarkable properties of these alloys to the attention of possible users outside of the dental field. The bibliography appended to the paper will prove of real value to those desiring definite data on this group of alloys.

As pointed out by the author some of these alloys, especially those designated as class 2 and class 3, possess unusually high strength, proportional limit and ductility, with the possibility of altering these properties by heat treatment. They are also highly resistant to corrosion. Another important characteristic which was not specifically mentioned is the relatively low modulus of elasticity, the modulus in tension ranging from about 40 per cent to about 60 per cent of that of steel. The combination of high proportional limit and low modulus of elasticity makes these materials exceptionally resilient and be-

[3]Technical Report No. 17192, General Electric Co., Schenectady, N. Y.

[4]Bulletin 4, "Ajax-Northrup Electric Furnaces," The Ajax Electrothermic Co., Trenton, N. J.

cause of this characteristic an alloy of this type has already been used for resilient springs in the construction of certain precision instruments. It is believed that as the unusual properties of these alloys become more generally known other advantageous applications will be found.

The author's discussion of heat treatment seems unfortunate since the data he presents are very indefinite and his brief quotations from and references to the Bureau of Standards reports do not present these reports in such a way that their true significance is readily understood. Most of the author's conclusions on the effects of heat treatment apparently are based on a few tests of a small group of alloys and these tests and alloys are not described in sufficient detail to permit interpretation of the data reported. For a more detailed discussion of this subject it is suggested that reference be made to Bureau of Standards Research Paper No. 32.

In Fig. 3, two photomicrographs are presented which, according to the accompanying legend, show platinum segregation in a piece of wire. The presentation of these photomicrographs without further comment might easily lead to the assumption that this is a common type of defect in the alloys discussed. This was formerly true and unfortunately such defects are still to be found in certain types of products. However, they are not at all likely to occur when the best modern manufacturing methods are employed.

Written Discussion: By E. M. Wise, research laboratory, International Nickel Co., Bayonne, N. J.

The author has carefully outlined some of the important characteristics which must be secured to render precious metal alloys useful for dental purposes, and has qualitatively indicated the role of the numerous metallic components of the orthodox dental alloys. The absence of quantitative data regarding the compositions of the alloys employed by the author is, however, unfortunate in view of the fact that the proper interpretation of some of the author's observations is impossible in their absence.

The influence of the addition of various metals upon the melting point, as shown in Fig. 1, indicates that the $\frac{\delta\ (\text{Added element})}{\delta\ (\text{MP})}$ is approximately constant for each of the several metals. Such a conclusion may be roughly valid for alloys containing large amounts of gold and the platinum metals, but obviously does not apply to alloys of special types, such as the solders and to some of the jewelry alloys, where the effect of increasing the copper may be to raise, rather than to lower, the melting point. In binary and higher order systems, characterized by a valley in the melting point composition domain, the influence of a variation of some one of the components upon the melting will change in sign at the bottom of the valley and will be zero at this point.

The optimum composition of an alloy designed for a specific purpose is dictated by many factors other than melting point, so that with the possible exception of solders, it is frequently necessary to consider the melting point per se as a compromise between what is desired and what results from other considerations.

In connection with previous metal solders, the effect of the addition of some of the plate being soldered upon the melting point of the solder is very im-

portant. The composition of the solder, and the plate with which it is used, should be such that a pick up of plate will increase the melting point of the solder. Such a combination permits the solder to flow over the surface in a thin layer without unduly attacking the surface being soldered.

The broad validity of Tammann's generalization regarding the relation between the atomic composition and the reactivity of alloys has been seriously questioned by careful workers, and their criticism has not been adequately met. In spite of this, it does appear that dental alloys should contain not less than some 50 atomic per cent of platinum, palladium, and gold, but not including silver, to give good satisfaction from the standpoint of tarnish and corrosion. In any event, the possible effects of residual coring in the case of castings, and of the influence of precipitation treatments upon the composition and reactivity of the phases present, should not be ignored when fixing the content of noble metal in a dental alloy.

Palladium has well established its position as a component of dental alloys through many years of use and some application is being made of alloys containing very large percentages of palladium with either little or no gold, so that its corrosion-resistance appears to be very substantial and quite adequate for dental service.

Silver is useful for the several reasons pointed out by the author, and is likewise effective, when used in the proper amounts, in increasing the tensile strength of the alloy. Its low cost and moderately good resistance to corrosion likewise justify its use.

In most of the gold-base alloys the hardening is due to the atomic rearrangement incident to the production of Au-Cu, but it is known that alloys quite free from gold but containing palladium or one of its allies and copper, with or without silver, are very responsive to heat treatment; likewise, the silver-rich copper-silver alloys are somewhat responsive to heat treatment. Furthermore, the binary gold-platinum alloys of suitable composition are responsive to precipitation heat treatments, so that the complexity of the problem becomes evident and the contribution of each element is not always clear.

With regard to the thermal domain of existence of the phase approximating Au-Cu, the recent work of Kurnakow and Ageew[5] has indicated that this phase may exist at temperatures as high as some 450 degrees Cent., which is considerably above the value of 371 degrees Cent. indicated by the author. This recent work likewise indicates that some discontinuity exists in the resistance composition isotherms at even higher temperatures.

Palladium, as the author states, is an effective whitener for gold-base alloys, but the amount required to produce "whiteness" depends very considerably upon the level of whiteness required. In some cases, quantities of the order of 20 per cent or more may be required to secure the desired color.

Copper seems to be the most satisfactory element for inducing precipitation hardening but, as stated earlier, the platinum-gold and other platinum alloys precipitation harden in the absence of copper.

The compounds Au-Cu, Pd-Cu and Pt-Cu present many analogies but do

[5]N. S. Kurnakow and N. W. Ageew, "Physico-Chemical Study of the Gold-Copper Solid Solutions," British Institute of Metals, Advance Copy No. 576, for presentation September 14-15, 1931.

not appear to be strictly isomorphous. Nevertheless, it is probable that they do exhibit considerable mutual solubility, and that the complex compounds containing the platinum metals are more satisfactory hardeners than the simple Au-Cu phase. Experience has indicated that the production of very high strengths, coupled with reasonable ductilities, requires the presence of one or more of the platinum group metals in the alloy.

The recent work of Röhl upon the alteration of the modulus of elasticity of gold-copper alloys by the heat treatment is interesting, for his results indicate that the modulus of an alloy having the composition Au-Cu may be reduced by 30 per cent through the production of the nonstatistical atomic arrangement stable at low temperatures. In practical dental and jewelry alloys the effect would be expected to be of much smaller magnitude but might be evident, and perhaps important, under special circumstances such as those encountered in the use of precious metal alloy springs for precision instruments.

With regard to Saldau's work on the Au-Zn alloys, in which he found solid-solid transformations to occur in alloys with a zinc content ranging from 13 to 31 atomic per cent, it should be borne in mind that he placed great reliance upon the changes in the electrical conductivity of the alloys with a change in temperature. The complicated and ill understood laws governing the conductivity of even solid solutions, much less intermetallic compounds, have been discussed in detail by Hume-Rothery, and further study might lead to some slight alteration in the interpretation of results obtained by this method.

With regard to the high nickel content gold alloys, the great loss in corrosion-resistance which results from long-time aging was pointed out by the discussor some years ago,[6] and is a very cogent reason for avoiding such treatments in the high nickel alloys.

With regard to the mode of heat treatment required to produce useful combinations of strength and ductility, the author's observations are interesting and pertinent. It is evident that one heat treatment could not be expected to produce optimum results when applied to all classes of material, particularly so when the maximum temperature attained during the low temperature treatment may, in certain cases, be above the domain of compound formation. In this event, the hardening must occur at a lower temperature and starts at some point during the cooling cycle.

The author's observations regarding the secular changes in strength are very interesting, but are rather difficult to account for in alloys which require a considerable elevation of temperature to cause precipitation to occur at a useful rate. The loss in strength observed with one alloy would indicate that this alloy over-aged, presumably at room temperature, while the other alloy had not yet reached its maximum aged strength during the slow cooling treatment and continued to age at room temperature. If the analyses of these alloys were given, a better appraisal of these experiments would be possible.

If these effects actually occur, it would be expected that a considerable increase in strength and hardness would be observed in alloys initially quenched from a high temperature and allowed to remain at room temperature for some

[6] E. M. Wise, "High Strength Gold Alloys for Jewelry and Age Hardening Phenomena in Gold Alloys," *Transactions*, Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers, 1929, p. 391.

time. I should like to inquire whether the author has any observations concerning this latter phenomenon.

The normal influence of even a small amount of cold work upon the age-hardening alloys is to considerably expedite the aging, and in practice age-hardening treatments are frequently applied to material which has been subjected to localized deformation with the result that the optimum precipitation treatment may differ in two portions of the same sample. In this connection, Kurnakow and Ageew found, by following the changes in the electrical resistance of a quenched sample approximating the composition Au-Cu, that the transformation appeared to start at about 125 to 150 degrees Cent. under the conditions of their experiments, but that the initiation of the transformation in a cold-worked wire appeared to start at a slightly higher temperature, i.e., 225 degrees Cent. The reason for this apparent increase in stability upon cold working is certainly not clear and is not in accord with the usual behavior of metastable systems. In their work there was a small difference in the behavior of an alloy reheated immediately after quenching and a similar sample quenched and allowed to lie at room temperature for a week before reheating. The aging of the sample tested immediately after quenching started at 125 degrees Cent. and was substantially completed at 200 degrees Cent., while the sample which had remained at rest for a week required a temperature of 150 degrees Cent. for initiating the transformation which was substantially completed at 350 degrees Cent. The presence of considerable stress in the sample tested immediately after quenching and the reduction of this stress on standing at room temperature might account for this behavior if the several runs were made under identical conditions with regard to the rate of heating. These experiments still leave the influence of cold work upon the stability of this type of alloy in an anomalous state which should be cleared up by further work.

The microstructural changes accompanying aging are difficult, or sometimes impossible, to follow in their early stages, but if alloys be used which are initially homogeneous, conditions are much more favorable for observing the aging process than they are in badly cored samples. This is somewhat unfortunate for the thermal treatments usually employed with dental alloys do not lead to the initial production of very homogeneous solid solutions prior to the aging treatment.

With regard to the methods employed for testing small wires, rods, etc., one very important factor involved is the straightness, or rather the lack of it, in the sample to be tested. This is rather obvious, but is perhaps not always appreciated. With straight wires of small diameter, the need for averaging the deformations occurring at both sides of the specimen is probably not great, and the additional weight and increase in the number of joints required for averaging seems hardly to be justified. A simple extensometer of the Anderson type is, with a few modifications, quite suitable.

In any case, the difficulty in determining some approximation to the true elastic limit (if it be greater than zero) of nonferrous alloys is considerable, and the personal errors are of large magnitude, so that some method for determining a value useful for design purposes is highly desirable. Variants of Johnson's method have been employed by several investigators, including the discussor, and are doubtless useful in furnishing design data. For this reason,

I am very glad that the present author has brought out the merit of the modified Johnson method as applied to torsion measurements.

One source of inaccuracy which becomes increasingly important as the size of the test sample is decreased, is the determination of the diameter of the wire. If the area of a wire approximately 0.040 inch in diameter is to be known within the limits ± ½ per cent, the diameter must be measured accurately within the limits ± ¼ per cent or to ± .0001 inch, a limit which is considerably beyond the limit of accuracy of the usual micrometer.

In the torsion device described by the author, the gage length employed appears to be about three quarters of an inch. It would seem that the use of such a short gage length would involve considerable uncertainty in determining the effective length of the specimen between the measuring arms. Another method for measuring the torsional modulus which has been used with considerable success by one of my associates, is that of the torsion pendulum. In this device the wire under test, which can be of considerable length, supports a circular disk of known moment of inertia at its lower extremity and restrains the angular displacement of this disk. The period of oscillation of the system can be determined with high accuracy, and from this value the modulus can be readily computed. This method has several advantages, one of which is that the modulus can be accurately determined without inducing very high stresses in the wire being tested. By arranging this device so that the amplitude of angular displacement is slowly increased by properly timed impulses of low energy, the stress at which the material begins to dissipate appreciable energy could readily be determined. This value is, perhaps, as good a criterion of the "elastic limit" in torsion as any. By starting with a high amplitude and observing the decrement somewhat similar results could be secured, but this procedure would involve some alteration in the properties of the wire, due to the high initial stress employed.

Oral Discussion

SAM TOUR:[7] I would like to ask Mr. Brumfield what proof he has that this hardening is due to the particular compositions which he is speaking of and not due to traces of other metals present. We know that many of our precious metal alloys are, roughly speaking, impure. The platinum alloys, for instance, often contain considerable of the other noble metals and very often we feel that these other metals are the hardening agents in heat treatment.

Author's Closure

The author's purpose in the writing of this paper was a general description of precious metal alloys. When specific properties of definite alloys have been referred to, such reference was in connection with the primary purpose rather than in an attempt to make a definite contribution to the knowledge of precious metal alloys. In view of this fact, the exact compositions of these alloys were not regarded as essential.

Since, however, these omissions have caused adverse comment in the discussion of the paper, the author has inserted the batch mix in all cases where definite properties of a given alloy have been referred to.

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[7]Vice-President, Lucius Pitkin, Inc., New York City.

The implied criticism carried in the term "practically hidden alloys" used in the discussion by the Bureau of Standards group deserves comment. It is true that most manufacturers of precious metal alloys have been reluctant to publish formulae of their alloys. They are justified in this attitude from a commercial standpoint on two counts. First, such publication exposes the manufacturer to cheap and unfair competition in view of the fact that the composing elements may be alloyed at low temperatures with comparatively inexpensive equipment. Second, there is a marked tendency among customers to haggle over price on a basis of the bullion value of the alloy when compositions are generally known.

The author is at a loss to understand the comment of the Bureau of Standards group in regard to the extensometer shown, which reads: "It is also suggested that those interested in securing most accurate values for percentage of elongation see Fig. 34 in Research Paper 32 for a double dial type extensometer." The author's confusion arises from the fact that these extensometers are never used to determine percentage of elongation in the engineering sense but only for elongations slightly beyond the elastic elongation. In any case the averaging type single dial instrument has been long used and proved in testing practice and has considerable advantage over the double dial type in convenience and rapidity in use. There is an adjusting screw on the extensometer shown in Fig. 5 to correct for lack of parallelism when elongations are excessive.

The statement that shearing properties are revealed by tensile tests implies rather more than the truth. In fact about the only bearing a tensile test has on shearing properties is to show comparatively the limiting ratio of true (not engineering) tensile and shearing strengths. Any torsion test will show as much concerning tensile properties.

It is true, as Mr. Coleman and Mr. Elliott suggest, that the inference should not be drawn, that such segregations as shown in Fig. 4 are common in commercial alloys. It was only shown to illustrate the limited use of the microscope in connection with these alloys.

In regard to the possibility of heat treatment being due to obscure impurities in the alloying elements, mentioned by Mr. Tour, I would say that was very remote. The first proof is given in Fig. 2. The second would be that if it were due to those obscure impurities in the alloying elements the heat treating reaction of the alloys would be very erratic, but they are not; they repeat themselves time after time. So certainly the heat treating reactions must be due to definite compositions which are very largely constant in the alloy.

The author's knowledge of and experience with gold alloys agrees in general with the comments of Mr. Wise, many of which are valuable. It is true as Mr. Wise suggests that the relationship between melting point and added element does not remain a straight line throughout the range of alloying possibilities. We have found the relationship nearly enough a straight line, however, when the range of alloying possibilities is limited, that the assumption that it is a straight line proves valuable for comparative purposes within the limited group. The fact that these relationships are not constant as between widely differing groups of alloys was the reason given in the paper for omitting the temperature scale from Fig. 1. In dental alloys it is true the melting point is not of controlling importance, yet there is usually a fairly definite limit for

melting point of these alloys, both upper and lower, fixed by the practicalities of their use.

The comment that there is a desirable relationship between the compositions of the plate and the solders which are used with it is true. The average manufacturer of dental alloys, both solders and plates, has little opportunity to make these relationships effective, however, because of lack of knowledge of or influence in the use of his materials by the consumer. Other factors such as soldering temperature, bulk of plate and time of completing the operation may affect results to such an extent as to submerge the most ideal relationships.

The author is in agreement with Mr. Wise that a precious metal content of 50 per cent or more on an atomic basis, is not an infallible criterion for resistance to corrosion in the mouth. He has in mind one alloy consisting of atomic percentages Au—58.2 per cent, Ag—22.6 per cent and Cu—19.2 per cent against which a number of definite complaints of mouth corrosion were registered. Another alloy consisting of atomic, Au—32.4 per cent, Ag—45.8 per cent and Pd—21.8 per cent is apparently giving satisfactory service, judged by the absence of complaints. In the case of the latter alloy, the precious metal content exclusive of the palladium is considerably below the limit set of 50 atomic per cent. Replying to the query by Mr. Wise, the author has made no experiments to determine possible changes in strength of quenched alloys resulting from a period of rest after quenching.

The point which Mr. Wise makes that test wires should be straight is well taken. Considerable thought and effort is justified in order to maintain straightness during the heat treating process. A curvature of about 25 inches radius in a test wire of 0.035 inch diameter induces bending stresses in the wire at about 5000 pounds per sq.in. maximum, on straightening during testing. Such stresses would not however affect the proportional limit by this amount because of their nonuniform distribution. Short bends in the test specimen are not as important as curvature which extends through the test piece.

The comments in regard to the accuracy of diameter measurements necessary to obtain errors in diameter not greater than $\pm$ ½ per cent are true of course. It is questionable however whether this degree of accuracy is justified in obtaining results which are to be used essentially for engineering design purposes. Other uncertainties connected with their use are much greater than the approximately one per cent error in area of test piece resulting from the $\pm$ ½ per cent error in diameter.

The torsion device shown will test on gage lengths up to 6 inches. The author usually uses gage lengths of about 1 inch. There is possibly an error of as much as one per cent in measuring such gage lengths. The author is opposed to gages of too great length for torsion testing because of column action resulting from the induced compression stresses. For our purposes the proportional limit in shear which is unaffected by gage length is more important than modulus of elasticity.

The pendulum device described by Mr. Wise for obtaining shearing moduli is interesting. Judging from comparisons of results obtained on materials for static tests and impact tests, the question arises as to whether results obtained with a constantly varying load such as the pendulum applies would be directly comparable to those obtained from static load tests.

BEHAVIOR OF SOME IRONS AND STEELS UNDER IMPACT AT LOW TEMPERATURES

By Robert Sergeson

Abstract

This paper gives the results of testing, under impact, certain irons and steels at low and subzero temperatures. For this purpose the Charpy impact testing machine was selected because of its ease and quickness of operation.

In general as the subzero temperatures are approached the impact values fall rapidly for notched wrought iron, carbon and alloy steels, with exception of the 3½ and 5 per cent nickel low carbon. Introduction of nickel into the spring steels increases their resistance at low temperature. The austenitic type of stainless iron is only slightly affected by subzero temperatures.

THOSE responsible for the designing and manufacture of the present day mechanical equipment are careful to understand, not only the chemical analyses of their materials, but also the physical characteristics. Perhaps this is shown most vividly in aviation. Both of the polar regions have been conquered by the air, and recently man has reached an altitude of ten miles. Certainly to accomplish such feats, the machines used have been subjected to extremes in temperatures. Railroads and the automobile each year push further in to the colder climates, and hence these industries have become alive to the effect of temperature changes on their equipment.

It is the purpose of this paper to present certain data with regard to impact properties of certain irons and steels at low and subzero temperatures. These data represent a summation of work done from time to time, and are not from a single investigation. The Charpy machine was selected for this work because of the rapidity with which tests may be carried out. Tests may be removed from the heating or cooling media and broken within two to three seconds. The Charpy machine used had a capacity of 305 foot pounds. Unless otherwise stated, all impact tests were 0.394 inch square by 2.165

A paper presented before the Thirteenth Annual Convention of the society in Boston, September 21 to 25, 1931. The author, Robert Sergeson, is a member of the society. He is associated with the metallurgical laboratories of the Republic Steel Corp., Canton, Ohio. Manuscript received June 19, 1931.

inches and notched with a special cutter having the same radius as standard drills commonly used. The area below the notch was standard.

Although the essential result obtained in impact testing is a measure of the energy absorbed by the test specimen while undergoing rupture or certain deformation, there is an additional factor which also should be considered, namely—the percentage of unbroken area. This was suggested by Mr. Miller.[1] For example, two steels may show the same impact resistance in foot-pounds, and yet one may be broken completely while the other may be held together by twenty per cent of area under the notch which remains unbroken. Certainly the latter specimen distributes the force of the impact to a greater degree than the former. In this investigation the unbroken area was determined in the following manner. The fracture of the partially broken Charpy test was heat tinted, the test was then cooled and completely broken. The area of the fresh fracture was estimated visually for the percentage of unbroken area.[2] The data presented is discussed in the following sequence:

Section 1. Wrought iron and some low alloy steels
Section 2. Carburized and hardened wrought iron, carbon and alloy steels in unnotched state
Section 3. Heat treated spring steels
Section 4. Certain stainless irons.

Section 1

Table I lists the analyses of specimens investigated in this sec-

Table I
Analyses of Specimens Tested

Type	Carbon	Manganese	Sulphur	Phosphorus	Silicon	Chromium	Nickel	Molybdenum
2 Per Cent Nickel	0.04	0.12	0.021	0.019	0.005	....	2.06	....
Carbon-Manganese	0.22	1.04	0.04	0.081	0.07	....	....	....
Nickel-Molybdenum	0.15	0.44	0.02	0.018	0.24	0.08	0.66	0.15
S.A.E. 2115	0.144	0.42	0.02	0.016	0.24	0.09	1.49	....
Wrought Iron Engine bolt								
Wrought Iron Chain bolt								

[1] H. L. Miller, metallurgist, Republic Steel Corporation, Central Alloy Division, Canton, Ohio.

[2] No bibliography is given on impact data as this is covered in the preprint of the "Symposium on Effect of Temperature on Properties of Metals," held in Chicago, June 23, 1931, issued jointly by the American Society for Testing Materials and the American Society of Mechanical Engineers.

tion. The specimens tested at low temperatures were immersed in a bath of methyl alcohol cooled with CO_2 snow to the desired temperature. The specimens were held thirty minutes at temperature and then broken. In this series, tests above room temperature were immersed in boiling water. Five specimens were broken at each temperature and curves drawn from the average of the readings. Before machining into impact test pieces, these materials were given the following heat treatments in ¾-inch round by 14-inch lengths.

		Brinell Hardness
2 Per Cent Nickel Iron	Normalized from 1625 degrees Fahr.	108
Carbon-Manganese	Normalized from 1625 degrees Fahr.	130
Carbon-Manganese	Water-quenched 1625 degrees Fahr. Tempered 1250 degrees Fahr.	185
Carbon-Manganese	Water-quenched 1625 degrees Fahr. Tempered 900 degrees Fahr.	237
Nickel-Molybdenum	Water-quenched 1625 degrees Fahr. Tempered 1250 degrees Fahr.	114
Nickel-Molybdenum	Water-quenched 1625 degrees Fahr. Tempered 1000 degrees Fahr.	159
S.A.E. 2115	As-Rolled	130
S.A.E. 2115	Water-quenched 1625 degrees Fahr.	387
S.A.E. 2115	Water-quenched 1625 degrees Fahr. Tempered 600 degrees Fahr.	340
S.A.E. 2115	Water-quenched 1625 degrees Fahr. Tempered 1200 degrees Fahr.	175
Wrought Iron	Engine Bolt As-Rolled	130
Wrought Iron	Chain Iron As-Rolled	96

The results of the above heat treatments on the different types are shown by the curves in Figs. 1, 2, 3, 4 and 5. From these curves it is seen that the 2 per cent nickel iron shows high notch toughness throughout the range tested. The carbon-manganese steel and wrought iron specimens both showed a marked falling off in impact values as the temperature fell below +32 degrees Fahr. It is evident that these types are not suitable for parts which are subject to heavy shock and exposed to winter weather.

The nickel-bearing types, nickel-molybdenum and S. A. E. 2115 showed excellent impact values even at temperatures well below zero. It is interesting to note that in the case of the S. A. E. 2115 series the impact values may be varied widely. The as-quenched specimens due to high internal strain show low impact values, while the quenched and tempered (1200 degrees Fahr.) specimens show high values. It is regretted that the tests on this latter analysis were completed without observing the percentage of unbroken area. The 2 per cent nickel iron showed an unbroken area of 20 per cent throughout the range of temperature used and the nickel-molybdenum steel likewise except below —30 degrees Fahr.

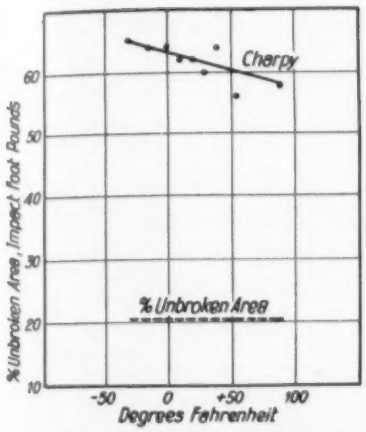


Fig. 1—Charpy Notched Impact Tests on 2 Per Cent Nickel Iron. Carbon 0.04, Manganese 0.12, Nickel 2.06. Normalized 1650 degrees Fahr. Brinell 108.

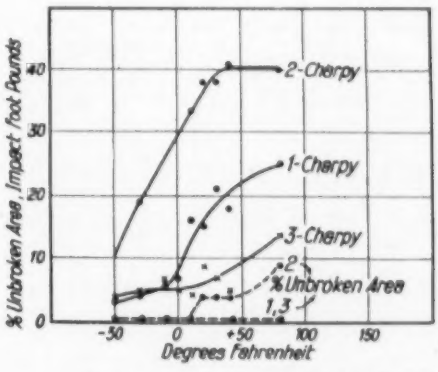


Fig. 2—Charpy Notched Impact Tests on Carbon-Manganese Steel. Carbon 0.22, Manganese 1.04, Silicon 0.07. 1. Normalized 1625 degrees Fahr., 130 Brinell. 2. 1625 degrees Fahr. Water, 1250 degrees Fahr. Air, 185 Brinell. 3. 1625 degrees Fahr. Water, 900 degrees Fahr. Air, 237 Brinell.

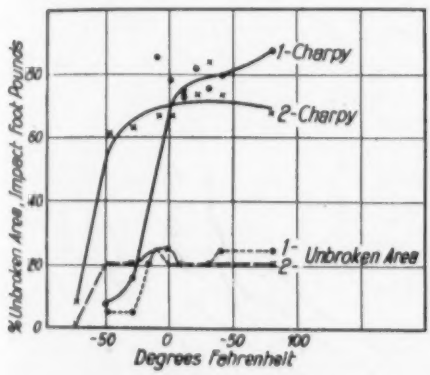


Fig. 3—Charpy Notched Impact Tests on Nickel-Molybdenum Steel. Carbon 0.15, Manganese 0.44, Nickel 0.66, Molybdenum 0.19. 1. 1650 degrees Fahr. Water, 1250 degrees Fahr. Air, 114 Brinell. 2. 1650 degrees Fahr. Water, 1000 degrees Fahr. Air. 159 Brinell.

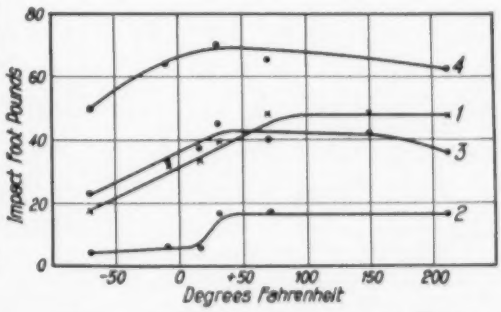


Fig. 4—Charpy Notched Impact Tests on S.A.E. 2115 Steel. Carbon 0.144, Manganese 0.42, Nickel 1.49. 1. As-Rolled 130 Brinell. 2. 1625 degrees Fahr. Water, 387 Brinell. 3. 1625 degrees Fahr. Water, 600 degrees Fahr. Air, 340 Brinell. 4. 1625 degrees Fahr. Water, 1200 degrees Fahr. Air, 175 Brinell.

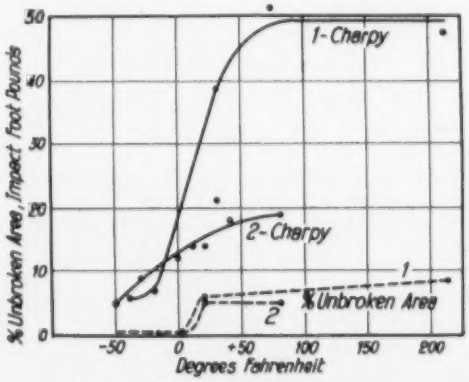


Fig. 5—Charpy Notched Impact Tests on Wrought Iron. 1. Wrought Iron Chain Stock, 96 Brinell. 2. Wrought Iron Engine Bolt, 130 Brinell.

The Canadian railroads have taken advantage of these properties and use many nickel-bearing steels on their locomotives, e.g., staybolts, engine bolts, boiler shells, etc.

That wrought iron is notch-brittle at low temperatures is generally known and guarded against by those who use chain. The fractures of the wrought iron impact tests were examined to note the type of break at fracture. Photomicrographs of specimens broken at —4 degrees Fahr. and 72 degrees Fahr., also photographs of the fractured Charpy tests are shown in Fig. 6. The specimens broken at low temperatures show the fracture to proceed along the grain boundaries with practically no distortion of adjacent grains. At room temperature and above, considerable distortion of grain is in evidence.

Section 2

Many carburized and hardened parts are required to withstand impact under varying temperature conditions. In view of this a series of tests were run to determine which grades of steel give the best impact resistance. The chemical analyses of the materials tested are shown in Table II. Unnotched Charpy tests were machined from hot-rolled bar stock and ground to 0.400 inch square. These specimens were subjected to the heat treatment shown in Table III, and then ground to 0.394 inch square to clean up after treatment, thus removing about 0.003 inch from surface of case on all sides. All tests were water-quenched and due to being unnotched, no cracking occurred.

Four impact specimens from each type were broken at 212, 75, 32, —16 and —70 degrees Fahr. All specimens were held 1 hour at temperature before being tested. Fig. 7 shows the results plotted from the average of four readings.

Fig. 8 shows one broken half of each half tested at 75 degrees Fahr. A group of tests from the 5 per cent nickel, 2 per cent nickel, plain carbon and wrought iron were arranged to show the difference in appearance of fracture with changing temperature. See Fig. 9. It will be noted from the chart that the plain carbon steel had a resistance of 45 ft.-lbs. at 212 degrees Fahr., but drops to 8 ft.-lbs. at 75 degrees Fahr. Examination of the fractures show a change from tough grain to a crystalline grain. The 2 per cent nickel iron remains tough at —16 degrees Fahr., but is crystalline at —70 degrees Fahr. Wrought iron is fairly tough at 75 and 212 degrees Fahr., but

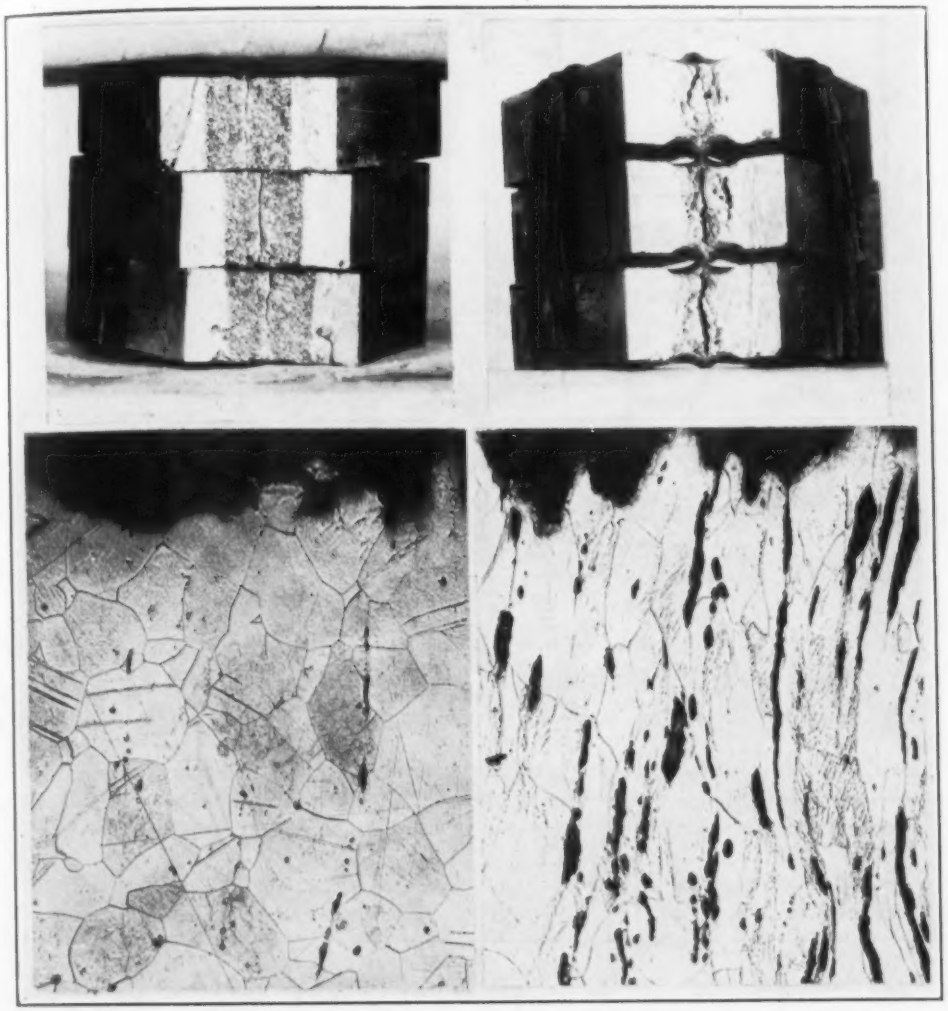


Fig. 6—Microstructure and Charpy Impact Tests of Wrought Iron Chain Stock at — 4 degrees Fahr. and + 72 degrees Fahr. Corresponding Charpy Impact Test Pieces Shown Above. Left — 4 degrees Fahr. Right + 72 degrees Fahr.

begins to show a crystalline structure at 32 degrees Fahr., and is completely crystalline with low impact resistance values at —16 degrees Fahr. and —70 degrees Fahr. The 5 per cent and 3½ per cent nickel steels remain tough all through the temperature range examined. The remaining types were crystalline when broken below 32 degrees Fahr.

Section 3

From previous work it has been shown that the introduction of nickel in steels increases their resistance to impact at low temperatures. The following work was conducted to determine the effect

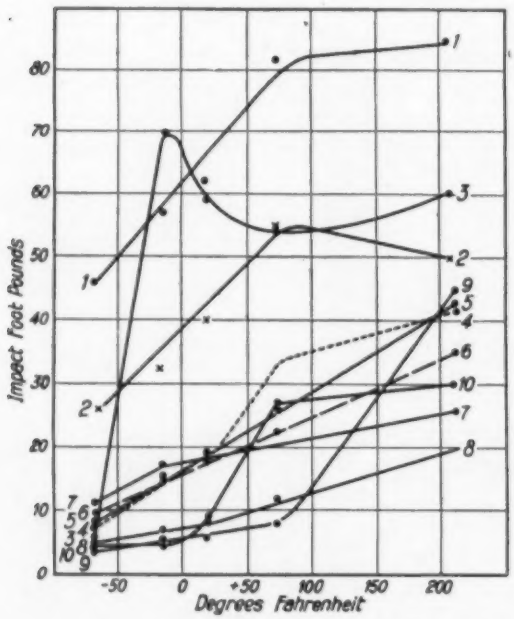
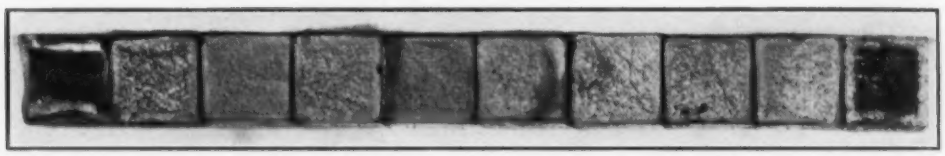


Fig. 7—Charpy Notched Impact Tests on Case Hardened Steels. All in Hardened State. 1. S.A.E. 2512; 2. S.A.E. 2315; 3. 2% Nickel Iron; 4. S.A.E. 6115; 5. S.A.E. 3115; 6. S.A.E. 4615; 7. 1.25 Chromium; 8. S.A.E. 5215; 9. S.A.E. 1020; 10. Wrought Iron.



Key No.	3	9	1	6	2	7	8	5	4	10
Ft.-Lbs.	54	8	82	23	55	20	12	26	33	27
Material	2% Ni.	1020	2512	4615	2320	1.25 Cr.	.75 Cr.	3115	6115	W.I.

Fig. 8—Charpy Impact Tests Showing Half of Each Bar.

of introducing nickel into spring steels. Table IV lists the preliminary analyses tested.

Tests were machined to 0.394 inch square by 2.165 inches long and left unnotched. All types were quenched in oil from above their respective critical temperatures and tempered to 387 Brinell hardness. This is the low-side hardness value for leaf springs. It was found by trial that only the carbon steels could be broken, others being too strong for the capacity of the Charpy machine. Izod notches were then cut in the test bars so that notch and the

Table II

Key No.	Type	Carbon	Manganese	Chromium	Nickel	Molybdenum	Vanadium
1	S.A.E. 2512	0.12	0.41	....	5.07	....	....
2	S.A.E. 2315	0.13	0.49	....	3.47	....	....
3	2 Per Cent Nickel Iron	0.04	0.12	....	2.06	....	....
4	S.A.E. 6115	0.135	0.47	0.95	....	....	0.18
5	S.A.E. 3115	0.155	0.51	0.51	1.24	....	....
6	S.A.E. 4615	0.17	0.45	....	1.59	0.27	....
7	1¼ Chromium	0.16	0.46	1.35	....	....	....
8	S.A.E. 5215	0.155	0.53	.74	....	....	....
9	S.A.E. 1020	0.16	0.46	....	....	....	....
10	Double Refined Wrought Iron						

Table III

Key No.	Carburizing Temp. Degrees Fahr.	Time in Hrs.	Requench Degrees Fahr.	Tempering Degrees Fahr.	Case Depth Inches	Rockwell "C" Scale
1	1650	4	1375	300	0.030	53-57
2	1650	4	1400	300	0.022	57-60
3	1650	5	Quenched from Pot	No	0.030	58-62
4	1650	4	1450	300	0.021	55-59
5	1650	4	1425	300	0.022	55-60
6	1650	4	1425	300	0.026	58-63
7	1650	4	1475	300	0.022	55-60
8	1650	4	1475	300	0.026	59-61
9	1650	4	1425	300	0.030	55-60
10	1650	5	Quenched from Pot	No	0.027	50-65

The 2 per cent nickel iron and wrought iron were carburized 1 hour longer than other types, because as a rule they do not absorb carbon quite as fast as regular steels.

Table IV

Type	Carbon	Manganese	Chromium	Nickel	Molybdenum	Vanadium
Carbon-Chromium	0.50	0.70	1.00	....	....	....
Chrome-Vanadium	0.45	0.82	1.03	....	....	0.17
Chromium-Nickel-Molybdenum	0.55	0.56	0.75	1.50	0.19	....
Silico-Manganese	Not analyzed					
Plain Carbon	Not analyzed					
Nickel-Molybdenum	0.50	0.45	....	1.50	0.16	....

Table V

Key No.	Type	Carbon	Manganese	Sulphur	Phosphorus	Silicon	Chromium	Nickel	Molybdenum	Vanadium
1	Plain Carbon	1.02	0.34	0.022	0.015	0.01	....	....	....	....
2	Chromium	0.49	0.85	0.022	0.022	0.15	1.14	....	....	....
3	Carbon-Silicon	1.00	0.32	0.020	0.017	0.39	....	....	....	....
4	Chrome-Vanadium	0.48	0.91	0.017	0.021	0.10	1.09	....	....	0.16
5	Chromium-Nickel-Molybdenum	0.51	0.60	0.020	0.017	0.25	0.95	1.93	0.25	....
6	Silico-Manganese	0.55	0.77	0.028	0.024	1.88	....	....	....	....
7	Nickel-Molybdenum	0.51	0.47	0.02	0.018	0.20	....	1.52	0.18	....
8	Nickel-Silicon	0.50	0.60	0.018	0.020	0.93	....	1.95	....	....

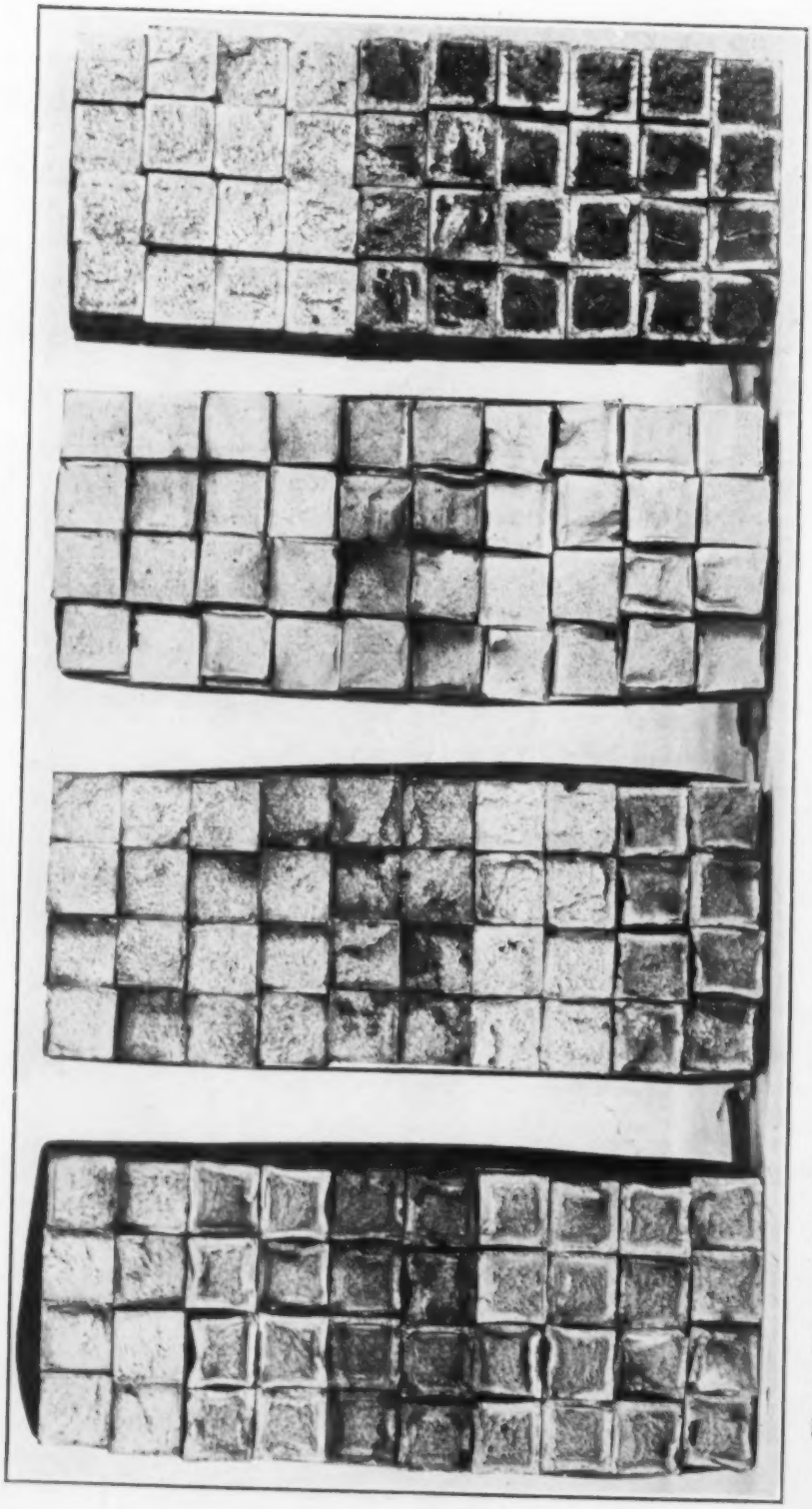


Fig. 9—Fractured Ends of Charpy Impact Test Bars of Four Different Materials. Left to Right 2% Nickel Steel; S.A.E. 1020 Steel; S.A.E. 2512 Steel; Wrought Iron. Temperature of Test Starting from Bottom Row Up. 1 and 2, 212 degrees Fahr.; 3 and 4 + 72 degrees Fahr.; 5 and 6, + 32 degrees Fahr.; 7 and 8, + 16 degrees Fahr.; 9 and 10, — 70 degrees Fahr.

amount of metal beneath it was standard for Izod tests. The tests were broken on the Charpy machine at four different temperatures and results recorded in Fig. 10. To recheck these preliminary results a second series of tests was run in which a larger number of steels were investigated. Table V gives analyses of steels tested.

These steels were rolled from 2½-inch square billets to regular No. 3 gage by 2 inches wide spring section. The chromium steel spring was taken from stock already rolled which was No. 3 gage but 1⅝ inches wide. Thus the steels could be said to all have had an equal amount of rolling effect. The test specimens were 0.250 inch by 0.395 inch by 2.165 inches long. Fifty pieces of each steel were treated. The heat treatment was arranged to give a Brinell hardness on the high side except for the carbon steel which was drawn to a lower Brinell number to improve the impact resistance, if possible. The specimens were held 30 minutes at temperature before quenching in oil and all were tempered by holding 45 minutes at temperatures. The following treatments were given.

Key No.	Type	Quenching Temperature Degrees Fahr.	Tempering Temperature Degrees Fahr.	Brinell Number	Brinell Number As-Rolled
1	Plain Carbon	1550	750	387–418	269
2	Chromium	1550	850	418	269
3	Carbon-Silicon	1550	800	430–444	302
4	Chromium-Vanadium	1550	800	444	302
5	Chromium-Nickel-Molybdenum	1550	800	444	351
6	Silicon-Manganese	1550	800	444	286
7	Nickel-Molybdenum	1550	750	418–430	248
8	Nickel-Silicon	1550	750	444	262

Five impact test specimens were broken at each temperature (212, 150, 75, 12, —15 and—50 degrees Fahr.). The averages of these were plotted as shown in Fig. 11. The nickel-molybdenum and nickel-silicon steels gave the best test results. On the Canadian National Railway carbon steel springs have been replaced on certain front end locomotive engine trucks with the nickel-molybdenum analysis. These springs have been in service during the past winter without any reported failures.

Fig. 9—Fractured Ends of Charpy Impact Test Bars of Four Different Materials. Left to Right 2% Nickel Steel; S.A.E. 1020 Steel; S.A.E. 2512 Steel; Wrought Iron. Temperature of Test Starting from Bottom Row Up. 1 and 2, 212 degrees Fahr.; 3 and 4 + 72 degrees Fahr.; 5 and 6, + 32 degrees Fahr.; 7 and 8, + 16 degrees Fahr.; 9 and 10, — 70 degrees Fahr.

Section 4

As the chief feature of the stainless metals is to resist one or more forms of corrosion it is to be expected that in many cases they will be subjected to the weather or other greater extremes in temperature. Hence the following stainless materials shown in Table

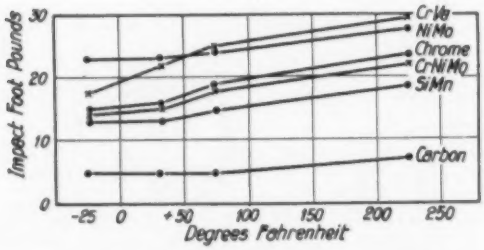


Fig. 10—Charpy Notched Impact Tests (Izod Notch) on Spring Steels. Test Bar Size 0.394 Inch Square by 2.165 Inch Long. Notched After Heat Treatment. All Brinelled 387.

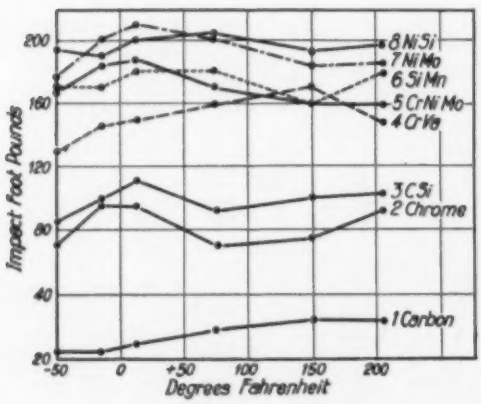


Fig. 11—Charpy Unnotched Impact Tests on Heat Treated Spring Steels. Test Bar Size 0.260 Inch by 0.335 Inch. Brinell Numbers: 1—378 to 418; 2—418; 3—430 to 444; 4—444; 5—444; 6—444; 7—418 to 430; 8—444.

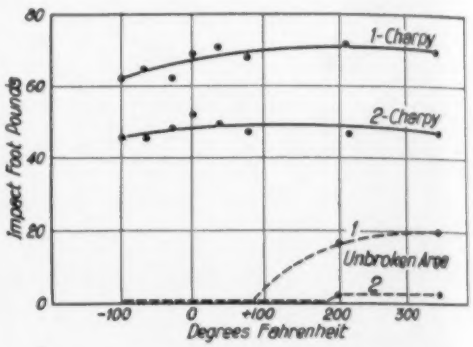


Fig. 12—Charpy Notched Impact Tests on Enduro KA2. Carbon 0.08, Chromium 17.52, Nickel 9.17.

1. 1950 degrees Fahr. Water, Brinell 143.

2. 1950 degrees Fahr. Water and Cold Drawn, Brinell 212.

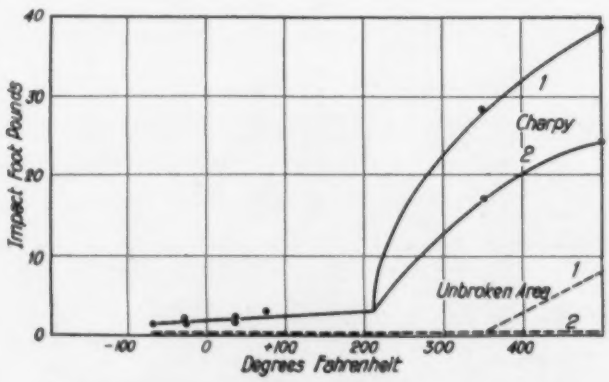


Fig. 13—Charpy Notched Impact Tests on Enduro AA. Carbon 0.08, Silicon 0.50, Chromium 17.95.

1. 1500 degrees Fahr. Air-Cooled, 149 Brinell.

2. 1500 degrees Fahr. Air-Cooled and Cold Drawn, 174 Brinell.

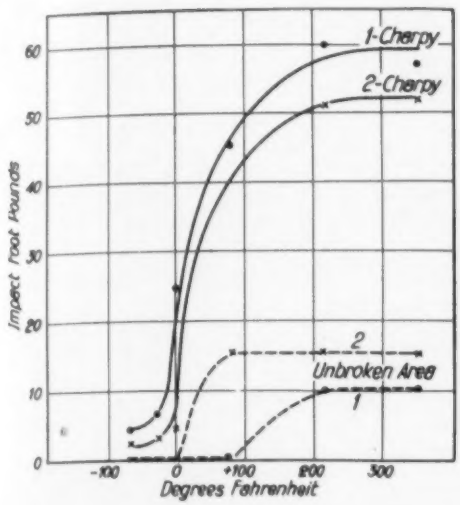


Fig. 14—Charpy Notched Impact Tests on Enduro S. Carbon 0.10, Chromium 13.31.
1. 1500 degrees Fahr. Furnace, 1200 degrees Fahr. Air, 146 Brinell.
2. 1500 degrees Fahr. Furnace, 1200 degrees Fahr. Air and Cold Drawn, 179 Brinell.

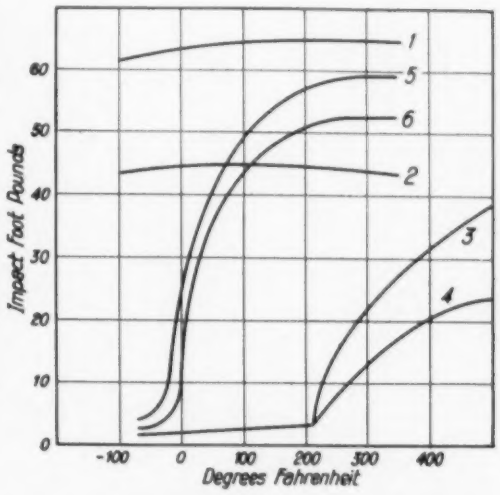


Fig. 15—Charpy Notched Impact Tests on Stainless Irons.
1. Enduro KA2, 1950 degrees Fahr. Water. 2. Same as 1 Cold Drawn. 3. Enduro AA Annealed. 4. Same as 3 Cold Drawn. 5. Enduro S Annealed. 6. Same as 5 Cold Drawn.

VI were studied for their impact properties at low temperatures. These materials were studied in treated and in the cold drawn condi-

Table VI

Type	Carbon	Manganese	Sulphur	Phosphorus	Silicon	Chromium	Nickel
A A	0.08	0.46	0.018	0.020	0.50	17.95	....
S	0.10	0.45	0.014	0.022	0.35	13.31	....
KA-2	0.08	0.35	0.013	0.019	0.57	17.52	9.17

tion. Bars $1\frac{1}{16}$ inch round were obtained in each analysis in the hot-rolled state; these were then heat treated as follows.

Key No.	Type	
1	KA-2	1950 degrees Fahr. Water quench to Brinell 143.
2	KA-2	1950 degrees Fahr. Water quench and Cold Drawn $\frac{1}{16}$-inch Draft —Brinell 212.
3	AA	1500 degrees Fahr. Air Cool to Brinell 149.
4	AA	1500 degrees Fahr. Air Cool and Cold Drawn $\frac{1}{16}$-inch Draft—Brinell 174.
5	S	1500 degrees Fahr. Furnace Cool 1200 degrees Fahr. Air Cool—Brinell 146.
6	S	1500 degrees Fahr. Furnace Cool 1200 degrees Fahr. Air Cool and Cold Drawn $\frac{1}{16}$-inch Draft—Brinell 149.

Charpy notched impact test specimens were machined from the center of the above treated types and two specimens were broken at each temperature investigated. Figs. 12, 13 and 14 show curves plotted from the average of the two readings. If results were not reason-

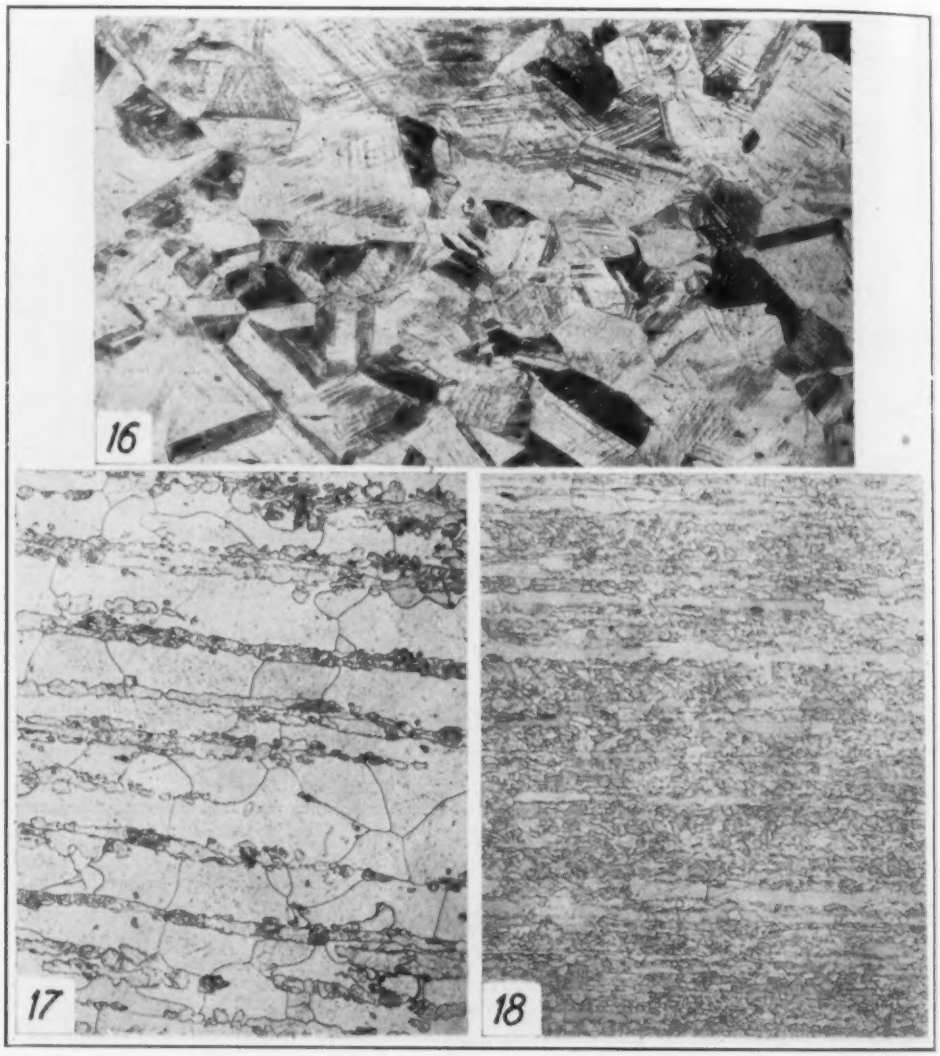


Fig. 16—Photomicrograph of KA2 Quenched in Water from 1950 degrees Fahr. and then Cold Drawn. × 100.

Fig. 17—Photomicrograph of Enduro AA Air-Cooled from 1500 degrees Fahr. and Cold Drawn. × 100.

Fig. 18—Photomicrograph of Enduro S Furnace-Cooled from 1500 degrees Fahr., 1200 degrees Fahr. Air-Cooled and Cold Drawn. × 100.

ably close additional tests were run. The values however, except in few cases, checked within 2-4 ft.-lbs. Fig. 15.

The structures of these types were examined in both treated and cold drawn state. In the case of the AA and S the cold drawing has not altered the structure while in case of the KA-2 the cold working is shown plainly. Photomicrographs of the cold drawn bars are shown in Figs. 16, 17 and 18.

The KA-2 austenitic types after being fractured were tested at

the fracture with a delicate magnet and were found to be increasingly sensitive to the magnet as the specimens were broken in order 72, 32, 0, —30, —70 and —100 degrees Fahr. The fractured specimens broken at 212 and 350 degrees Fahr were nonmagnetic at the fracture. The phenomenon is probably due to the fact that as the temperature falls the stress concentration becomes localized at the notch and the greater the cold work locally at the point of fracture, the more magnetic. Microscopic examination gave no evidence of martensite forming even at the lowest temperature. Excellent toughness is shown by this type throughout the range tested.

The type AA shifts the curve to the right and the crystalline fracture and brittleness is not removed until the temperature of 350 degrees Fahr. is approached. Hence this type should be used at slightly elevated temperatures if subject to shock. Such an application has been tried with this type (with silicon at 1 per cent) in locomotive firebox side sheets. After 72,000 miles the sheet was in perfect condition but on shop inspection was found to be cracked at staybolt holes. This was caused by the driving of bolts while the sheet was cold. A second set of side sheets are now being tested in service. These have served for approximately 24,000 miles. When staybolts are renewed or sheets are to be hammered to remove scale deposits, the sheets should be heated first to approximately 300 degrees Fahr. at which temperature the steel is tough.

Type S shows intermediate values and falls off rapidly as zero temperature is approached. Cold working lowers the impact resistance and shifts the curve to the right. The amount of shift probably depends upon the amount of cold work.

Summary

Properly treated nickel-molybdenum (0.15 per cent carbon), S.A.E. 2115 and 2 per cent nickel iron show excellent notched impact resistance at subzero temperatures. Wrought iron and carbon-manganese steel show a marked falling off in notched impact resistance as zero degrees Fahrenheit is approached.

Unnotched carburized and hardened specimens of various carburizing grades when tested under impact show that the 5 per cent and 3½ per cent nickel steels and the 2 per cent nickel iron possess superior qualities, especially at the subzero temperatures.

Of the various spring steels, namely; carbon, carbon-silicon,

chromium, chromium-vanadium, silico-manganese, chromium-nickel-molybdenum, nickel-molybdenum and nickel-silicon, the latter two show the highest impact resistance throughout the temperature range examined. The carbon steel showed lowest.

Of the stainless irons studied, the KA-2 showed excellent impact resistance even to —100 degrees Fahr. The type AA shows a decided brittleness until temperature is raised to 350 degrees Fahr. at which temperature toughness is gained. The type S lies in between the KA-2 and AA.

ACKNOWLEDGMENT

The writer wishes to thank Messrs. H. L. Miller, Wilbur E. Warne and E. Rowland of the metallurgical laboratory of the Central Alloy District of the Republic Steel Corporation for their assistance in preparing the data for this paper.

DISCUSSION

Written Discussion: By J. F. Cunningham, superintendent engineering testing laboratories, Civil Engineering Dept., University of Manitoba, Winnipeg, Canada.

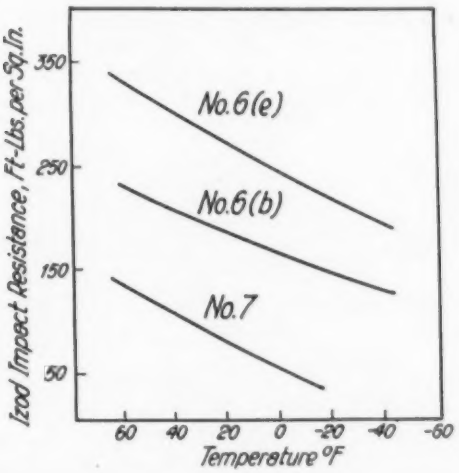
This excellent paper giving physical properties in impact at sub-zero temperatures of a large range of irons and steels adds greatly to the small amount of data available on the subject. It also shows the value of gathering periodically, under one heading, the figures obtained from time to time.

It is not possible to compare actual results as all the writer's information is obtained with an Izod machine. Prof. Moffatt's[1] figures do show that resistance to impact at low temperatures is higher for heat treated alloy steels than for plain carbon steels, when used for castings. Also that down to —36 degrees Fahr. (—38 degrees Cent.) a decrease of 10 to 11 per cent resistance to impact was found for steels containing 1.56 per cent nickel and 0.10 per cent vanadium and 2.69 per cent nickel respectively, whereas other alloys showed a decrease of 29 to 32 per cent.

The writer would not feel confident in using the results given in Fig. 1, as in no case of the many analyses of irons and steels in various physical conditions tested has he found the impact resistance increasing with decrease of temperature but always vice versa. The addition of nickel to iron should raise the impact values but the trend of the curve might be expected to remain the same.

Fig. 2 compares well with attached curves reproduced from Prof. Moffatt's work but the writer still considers that there is a low resistance or cold brittle point between the increments of temperature given.

[1]R. W. Moffatt. "The Effect of Low Temperatures upon the Impact Resistance of Steel Castings," *Canadian Journal of Research*, Vol. 2, May, 1930.



The curves on stainless irons are interesting and the conditions reached should be very useful to the designer.

Written Discussion: By C. C. Henning, metallurgist, Pittsburgh Works, Jones and Laughlin Steel Corporation.

Mr. Sergeson's paper contains some very interesting data on the important subject of the behavior of various steels under dynamic stresses at low temperatures. The data, as the author points out, represents a summary of work done from time to time and is not from a single investigation. The material used, therefore, was probably steel that was available and, consequently, was perhaps not always entirely representative of the grade.

It appears to the writer that at least this might have been true of the carbon-manganese steel. On this sample Mr. Sergeson has based his statements that carbon-manganese steel showed a marked falling off in impact values as the temperature fell below 32 degrees Fahr. and has concluded that this type is not suitable for parts which are subject to heavy shock when exposed to winter weather.

Analysis of this steel as given in Table I shows manganese 1.04 per cent which could hardly be classified as representing what is properly known as a carbon-manganese grade steel. The carbon-manganese grades usually contain a manganese content of 1.25 and over. Also 0.081 per cent phosphorus content is reported for this steel as compared to values under 0.020 per cent for the other grades involved. If this is the actual phosphorus content of this steel it would seem to us that this element offers far more reason for the drop in impact resistance at low temperatures than does the manganese content. We might suggest also that for a basic open-hearth steel to show a phosphorus content of this order would be evidence of improperly made steel and it would be manifestly illogical and improper to indict the carbon-manganese steels on the basis of steel represented by the analysis shown.

A recent investigation of the impact qualities at low temperatures of a carbon-manganese steel, 0.10 to 20 per cent carbon, 1.25 to 1.55 per cent manganese, 0.04 per cent phosphorus, 0.075 to 0.150 per cent sulphur, revealed desirably high and uniform Izod results on tests made within a temperature range

of 80 to —110 degrees Fahr. These tests were not heat treated but represented hot-rolled material. A comparison of the average Izod impact results obtained on this carbon-manganese steel and S.A.E. 1020 grade is shown below.

Temperature of Tests	Energy Absorption in Foot Pounds	
	S.A.E. 1020	Carbon-manganese Grade
80 degrees Fahr.	49	59
30 degrees Fahr.	50	62
—110 degrees Fahr.	10	61

It is evident that under the conditions of this particular investigation superior results were obtained on the standard carbon-manganese grade over the plain carbon steel with normal magnanese content which suggests that the element manganese within the range indicated above is beneficial toward the performance of steel under impact at low temperatures.

G. H. WRIGHT:[1] I would like to ask Mr. Sergeson if the failures in service were of a progressive type or of a sudden rupture type?

J. C. HODGE:[2] Some time ago we were called upon to investigate the physical properties of metals at a temperature of —110 degrees Fahr. (—80 degrees Cent.). The following metals and alloys were investigated: (1) 0.20 to 0.30 per cent carbon steel (firebox plate), (2) low carbon weld metal, (3) copper, (4) nickel, (5) monel metal, (6) Nirosta 18-8, (7) aluminum, (8) duralumin. The impact resistance at —110 degrees Fahr. of the two low carbon steels as represented by the firebox plate and by the weld metal was negligible, representing but 3 to 5 per cent of their impact resistance at normal temperatures. All of the other metals and alloys on the other hand maintained their impact resistance at —110 degrees Fahr., in fact the impact resistance of copper at the low temperatures was twice that at normal temperatures.

Author's Closure

I wish to thank Mr. Cunningham for his helpful discussion. It is pleasing to learn of Dr. Moffatt's results with alloy castings indicating the effect of nickel. The curve of the 2 per cent nickel iron (Fig. 1, page 371) does show an upward trend as the temperature decreases. This, however, is again shown when testing the same analysis in the carburized and hardened state, see Fig. 7. This rise is not excessive and may or may not be a characteristic of the iron. Additional tests were not made to check this trend as only the general characteristics of the iron were desired at the time of testing.

Mr. Henning's comments are indeed appreciated and I am very glad he has come forward to defend, and correct, the impression given, regarding the carbon-manganese steel. The high phosphorus content of steel given in this paper was responsible to a major extent to the low impact values. The values shown by Mr. Henning certainly suggest that the various carbon ranges of the manganese steels be investigated.

In reply to Mr. Wright's question I would say that most all spring failures that I have seen have been progressive or fatigue breaks, unless the material, of course, was badly mistreated.

Mr. Hodge's statements are of general interest and a valuable contribution.

[1]Testing laboratories, General Electric Co., Schenectady, N. Y.

[2]Babcock and Wilcox Company, Barberton, Ohio.

NATURE OF ABNORMAL GRAIN GROWTH IN HIGH SPEED STEEL

By G. R. Brophy and R. H. Harrington

Abstract

New data shows that the coarse-grained structure, formerly termed "fish-scale" or "marble fracture," is caused by application of the general laws for the production of abnormal grain growth. Strains of varying degree have been studied in relation to this abnormal grain growth. These strains are probably the result of composition gradients occurring in the cored grain structure. The brittleness of the coarse-grained material is excessive without any material difference in hardness from the normally hardened steel. It appears as if the utility of high speed steel as a tool material depends upon its heterogeneous character.

In a previous publication[1] it was shown that fish-scale is but an example of abnormal grain growth in critically strained austenite. A brief review of the more salient points is pertinent.

It was found that strains might be produced in austenite by heat treatment or by mechanical work above certain minimum temperatures, and that subsequent heating to some elevated temperature, termed the germinative temperature, caused a rapid and excessive growth of grains. The extent to which growth occurred, or the size of grains, was dependent upon the degree of strain produced. The best insurance against this defect was found to be thorough annealing just previous to the hardening.

Since it has been established that this fish-scale, or marble, fracture is abnormal grain growth it seems well to refer to it, in the future, by its rightful name.

The present paper describes an extension of the original work and brings out further proof. Some interesting and unexpected re-

[1]G. R. Brophy, R. H. Harrington, A. W. Merrick, "Occurrence of Fish-Scale in High Speed Steel," Transactions, American Society for Steel Treating, Vol. 18, 1930.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25. 1931. The authors are members of the society and are associated with the research laboratories of the General Electric Co., Schenectady, N. Y. Manuscript received June 16, 1931.

versals of tendencies have been found which lend themselves to intriguing speculations.

Materials Used

Since grain growth is most common to the lower tungsten high speed steels, this work was limited by choice to data obtained from the 14 per cent tungsten class. Two steels were used, each from a different source; one contained 2 per cent vanadium, ⅜-inch square, and the other 1 per cent vanadium, ½-inch square, with chromium about 4 per cent in each.

Program of Heat Treatments

Since the phenomenon we are dealing with is one of grain growth, it would follow that, as the strain introduced increased, lower germinative temperatures should be found.

Two sets of samples of each steel were strained, one set by air cooling and the other by water quenching from 800, 850, 900, 950, 1000, 1100, 1200, and 1275 degrees Cent. (1470, 1560, 1650, 1740, 1830, 2010, 2190, and 2325 degrees Fahr.). One sample from each set and each straining treatment was then quenched in oil from 1050, 1100, 1150, 1200, 1250, and 1275 degrees Cent. (1920, 2010, 2100, 2190, 2280, and 2325 degrees Fahr.). The samples were then notched, fractured, type of fracture noted, and Rockwell hardness taken. All samples were then drawn at 580 degrees Cent. (1075 degrees Fahr.) and the hardness again taken.

The two rates of quenching from the straining temperature were given in order to produce two degrees of strain from each temperature. Differences in germinative temperatures and grain size might then be expected.

Results

14-4-1 Steel—one-half inch square

Fig. 1 shows the fractures of the straining and hardening program as applied to this steel. These samples were air-cooled from the various straining temperatures. Table I gives a description of the amounts and comparative grain sizes[2] of the abnormally coarse

[2]Abnormal grain growth indicated by "G. G.—coarse—fine, etc."

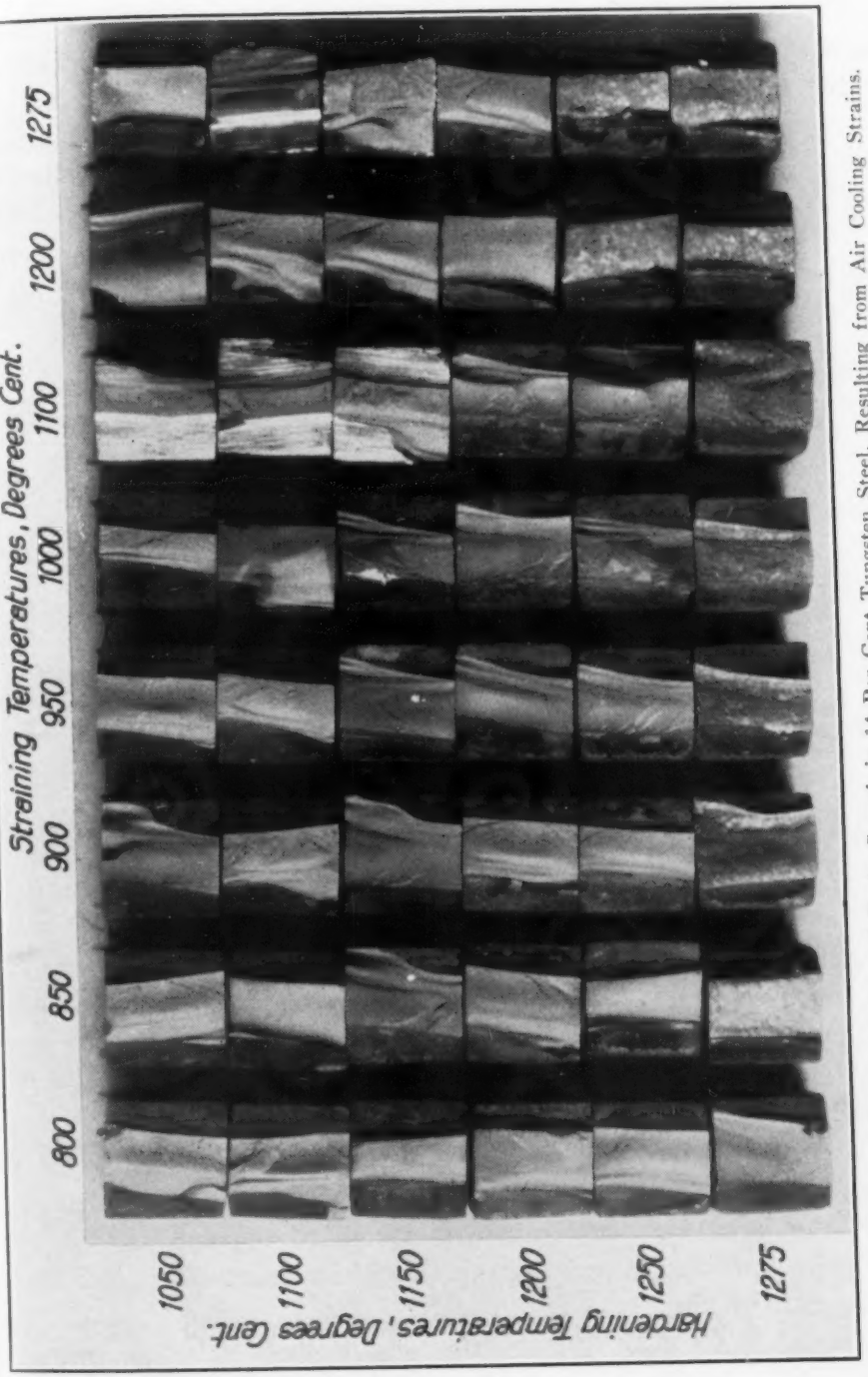


Fig. 1—Development of Abnormal Grain Growth in 14 Per Cent Tungsten Steel, Resulting from Air Cooling Strains.

grain as shown by these samples. Two hardness figures are given for each treatment, the upper figure in the table being the hardness of the sample as hardened and the lower figure being the hardness of the sample after a draw at 580 degrees Cent. (1075 degrees Fahr.). It is at once apparent that the hardness values bear no indication of abnormal grain growth.

Reference to Table I and Fig. 1 yields the interesting information that all straining temperatures produce sufficient strains to cause

TABLE I

HARDENING TEMPERATURES	TEMPERATURES OF STRAINING TREATMENTS-AIR COOLED							
	800°	850°	900°	950°	1000°	1100°	1200°	1275°
1050°	50.8 45.8	51.5 48.4	50.7 50.6	51.7 48.3	50.4 48.8	55.2 52.1	53.6 52.8	52.7 52.9
1100°	56.3 51.0	56.3 53.3	56 54	57.9 51.8	57.1 54.2	55.1 53.7	52.8 54.9	53.3 53.6
1150°	60.2 54.1	59.0 56.8	59.8 55.2	59.5 57.2	58.1 58.5	54.8 57.9	56.4 56.6	52.2 52.4
1200°	61.9 58.3	59.3 58.3	60.8 59.1	61.4 59.8	62.0 60.5	59.6 58.4	59.1 58.3 TRACES OF G.G.	58.2 59.6
1250°	63.6 62.2	61.5 61.2	62.2 60.9	61.6 62.3	61.3 61.6	62.5 60.2 75% OF G.G.	59.3 60.0 100% OF G.G.	61.6 61.3 COARSE G.G.
1275°	61.8 60.8 TRACES OF G.G.	62.6 63.8 100% OF G.G.	62.4 63.3 COARSE G.G.	63.5 63.9 COARSE G.G.	63.3 63.6 COARSE G.G.	61.7 63.4 COARSE G.G.	62.5 61.8 COARSE G.G.	61.2 62.9 COARSE G.G.

growth at 1275 degrees Cent. (2325 degrees Fahr.), although the 800 degrees Cent. (1470 degrees Fahr.) strain causes but a trace, and as the straining temperature increases to 1200 degrees Cent. (2190 degrees Fahr.) the germinative temperature decreases to 1200 degrees Cent. (2190 degrees Fahr.). This is in accordance with the law of grain-growth which requires that as strains increase the germinative temperature decreases. However, it seems peculiar that, when the straining temperature is increased beyond 1200 degrees Cent., the germinative temperature should increase. This indicates a reduction in strain.

Fig. 2 and Table II show the results obtained when this steel was strained by water quenching from the various temperatures. It is probable that the strains are greater than when introduced by air-cooling.

No grain-growth occurred at 1275 degrees Cent. (2325 degrees

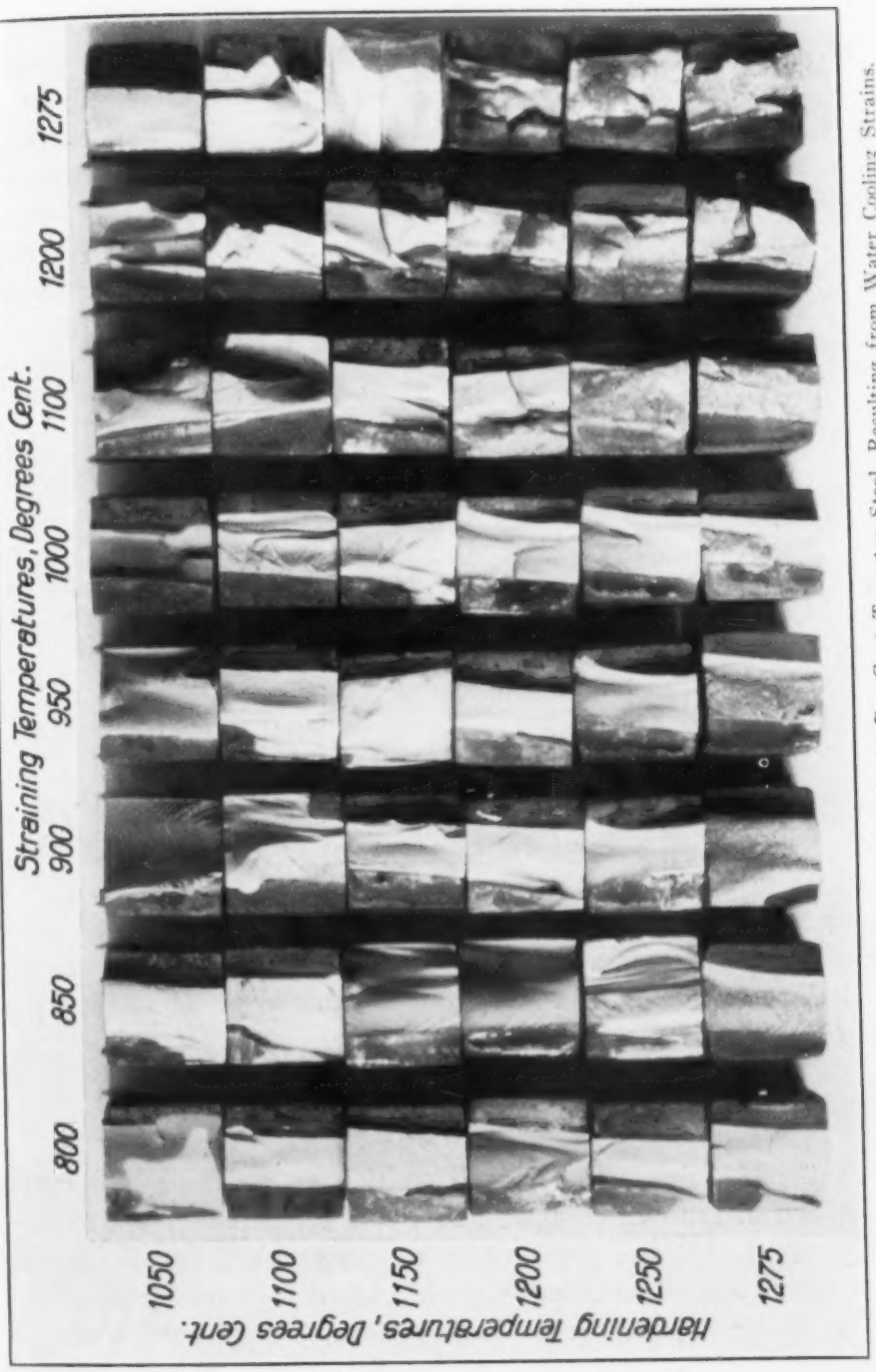


Fig. 2—Development of Abnormal Grain Growth in 14 Per Cent Tungsten Steel, Resulting from Water Cooling Strains.

Fahr.) in this series until a straining temperature of 850 degrees Cent. (1560 degrees Fahr.) was reached, but as in the previous series the germinative temperature decreases with increasing straining temperature. Again the limiting germinative temperature is 1200 degrees Cent. (2190 degrees Fahr.). Now straining from 1275 degrees Cent. (2325 degrees Fahr.) causes growth at 1200 degrees Cent. whereas in the corresponding air-strained sample no growth

TABLE II

HARDENING TEMPERATURES ↓	TEMPERATURES OF STRAINING TREATMENTS - WATER QUENCH							
	800°	850°	900°	950°	1000°	1100°	1200°	1275°
1050°	55.0 50.3.	56 50	54.6 50.9	53.5 50.0	55.2 51.3	55.2 51.0	53.2 50.8	52.7 51.1
1100°	58.5 54.8	54.8 54.0	57.2 55.0	58.2 55.2	55.4 54.3	54.4 54.2	51.4 52.2	53.3 51.3
1150°	60.2 57.9	60.4 58.1	60.3 56.4	61.1 57.5	58.2 57.7	59.2 56.1	58.4 55.2	55.6 55.9
1200°	62.0 58.5	60.7 60.2	62.0 59.4	61.4 59.0	62.5 59.8	61.6 59.9	60.2 59.9 FINE G.G 100%	61.2 59.9 COARSE G.G 100%
1250°	64.2 62.6	63.3 61.6	61.7 60.8	62.3 60.5	63.0 61.3	61.3 60.6 MEDIUM G.G 100%	61.0 61.3 MEDIUM G.G.	61.0 61.3 COARSE G.G.
1275°	62.4 63.2	62.2 62.9 FINE G.G 100%	62.0 62.7 FINE G.G.	61.7 63.2 FINE G.G.	62.3 63.5 MEDIUM G.G.	61.4 63.4 MEDIUM G.G.	62.3 60.7 COARSE G.G.	61.7 62.5 COARSE G.G.

occurred. Thus it is probable that water straining produces greater strains than does air straining. There is also a general tendency for the grain size of the water-strained samples to be smaller, probably resulting from the greater strains.

14-4-2 Steel—three-eighths inch square

Table III shows the data from the air straining program of this steel and is to be compared to Table I for the 14-4-1 steel. It is significant that the germinative temperatures differ for the two steels when treated identically, grain growth not occurring at 1275 degrees Cent. (2325 degrees Fahr.) for this steel until a straining temperature of 900 degrees Cent. (1650 degrees Fahr.) was used. Again 1200 degrees Cent. (2190 degrees Fahr.) appears as the limiting germinative and straining temperature.

Table IV shows the data from the water-strained group. This

TABLE III

HARDENING TEMPERATURES	TEMPERATURES OF STRAINING TREATMENTS - AIR COOLED							
	800°	850°	900°	950°	1000°	1100°	1200°	1275°
1050°	46.0 47.8	49.0 50.3	49.3 49.7	48.2 50.2	50.1 49.3	53.7 52.7	52.8 53.7	
1100°	51.7 49.5	51.3 50.5	50.3 48.7	49.7 49.6	51.0 52.0	53.1 54.6	57.3 54.2	52.5 54.8
1150°	55.7 53.5	56.6 53.1	51.8 52.5	50.3 52.7	53.7 53.1	56.6 57.7 TRACE G.G.	58.9 56.5	59.0 57.9
1200°	60.7 57.2	61.0 58.5	59.8 57.8	59.3 55.7	60.7 56.5	61.4 59.3 G.G. 100%	60.3 60.3 G.G. 100%	60.7 60.5
1250°	62.7 62.3	64.0 62.7	63.5 60.9 TRACES G.G.	64.3 62.4 G.G. 100%	64.3 60.5 G.G. 100%	62.3 61.4 G.G.	63.1 61.9 G.G.	61.8 61.5 G.G. 100%
1275°	64.3 62.2	65.3 63.3	64.3 62.7 G.G. 100%	63.6 63.0 G.G.	63.7 61.0 G.G.	61.9 61.5 G.G.	64.6 62.7 G.G.	62.5 61.5 G.G.

TABLE IV

HARDENING TEMPERATURES	TEMPERATURES OF STRAINING TREATMENTS - WATER QUENCH							
	800°	850°	900°	950°	1000°	1100°	1200°	1275°
1050°	51.0 50.6	48.6 47.1	47.4 46.3	49.3 48.4	50.9 51.7	50.4 47.5	51.7 53.4	50.9 51.9
1100°	50.0 50.3	47.7 48.9	51.0 50.8	47.6 48.2	50.6 48.6	51.9 53.4	53.6 53.7	53.9 54.4
1150°	56.9 57.0	57.3 56.3	55.0 55.1	55.8 53.2	53.7 53.5	52.7 53.4	57.9 56.9 TRACES G.G.	55.6 57.0
1200°	60.9 58.3	62.5 59.6	59.6 58.0	62.5 59.0	59.3 59.2	59.6 59.7	60.9 59.3 G.G. 100%	60.9 60.8 G.G. 100%
1250°	63.5 60.4	63.4 60.2	61.2 59.8	62.3 60.5	58.7 61.1	59.3 60.8 TRACES G.G.	62.7 62.0 G.G. 100%	58.1 60.9 G.G.
1275°	64.7 61.8	63.2 62.3	64.2 62.5	64.3 64.3 VERY FINE G.G. 100%	64.0 64.2 G.G. 100%	62.5 62.7 G.G. 100%	63.3 63.2 G.G.	61.3 61.9 G.G.

group shows the same variations from Table III that groups 2 and 1 show.

The Influence of Sample Size

(1) Although the two steels dealt with are of the same tungsten content, reference to Tables I and III will show that the first steel gave traces of abnormal grain growth at 1275 degrees Cent.

(2325 degrees Fahr.) as a result of air cooling from a straining temperature of 800 degrees Cent. (1470 degrees Fahr.), while the second steel required air cooling from 900 degrees Cent. (1650 degrees Fahr.). Tables II and IV show the results obtained from straining the same two steels by water cooling from the straining temperatures. As before, the second steel required a higher straining temperature to produce growth at 1275 degrees Cent. (2325 degrees Fahr.). It will be remembered that the samples of the first steel were of one-half inch cross-section as compared to three-eighths inch for the second steel.

Samples of the first or 1 per cent vanadium steel were then ground to ⅜ inch cross-section, annealed, and air-cooled from 800 850, 900, and 950 degrees Cent. (1470, 1560, 1650, and 1740 degrees Fahr.). These samples were then hardened from 1275 degrees Cent. (2325 degrees Fahr.) and fractured. Abnormal grain growth did not appear now until the steel had been strained from 900 degrees Cent. (1650 degrees Fahr.). This checks the 2 per cent vanadium steel. We, therefore, see that the size of the sample rather than the vanadium content is probably a factor in the production of strains and abnormal grain growth.

Effects of Straining and Hardening Treatments on the Impact Toughness of the Steel

During the fracturing of these samples it was often noticed that those showing abnormal grain growth seemed to be unusually brittle. It was decided to obtain impact values upon a series that was treated according to a similar program. The 14 per cent tungsten, 1 per cent vanadium steel was used. The straining was done by air cooling samples from 800, 850, 900, 950, 1000, 1100, 1200, 1250, and 1300 degrees Cent. (1470, 1560, 1650, 1740, 1830, 2010, 2190, 2280, and 2370 degrees Fahr.). The following hardening temperatures were used: 1100, 1150, 1200, 1250, and 1300 degrees Cent. (2010, 2100, 2190, 2280, and 2370 degrees Fahr.). A sample size of two inches in length by a 0.400 inch square cross-section was used and the bars were unnotched. Use of this size of sample also afforded a close check on the similar program applied to the samples of 14 per cent tungsten, 2 per cent vanadium steel of ⅜ inch cross-section.

Fig. 3 is the photograph of the fractures. Table V gives the

Fig. 3—Fractures of Impact Series 0.400 Inch Square Bars.

TABLE V

HARDENING TEMPERATURE	TEMPERATURE OF STRAINING TREATMENTS - AIR COOLED.									
	800°C	850°	900°	950°	1000°	1100°	1200°	1250°	1300°	1350°
1100°C	45	32	30	33	64	13	6	43.5	4.5	
1150°	99	55	30	62.5	18.5	76	19.5	37	13.5	
1200°	27	33.5	41	44.5	18	5.5 100% MEDIUM G.G.	6 100% MEDIUM G.G.	24	29	
1250°	55	18.5 CRACKED	54	63.5 30% COARSE G.G.	13.5 100% COARSE G.G.	9 100% MEDIUM G.G.	18 100% MEDIUM G.G.	20.5 100% VERY COARSE G.G.	29	
1300°	28	23	7.5 100% COARSE G.G.	16 100% COARSE G.G.	13.5 100% COARSE G.G.	11 100% FINE G.G.	9 100% FINE G.G.	7 100% VERY COARSE G.G.	8.5 100% VERY COARSE G.G.	FINE GRAINED NO G.G.
1350°	COMPARATIVE IMPACT VALUES OF FINE AND COARSE GRAINED STEEL. FOOT POUNDS ABSORBED IN FRACTURING .400 SQ. BARS. THREE ADDITIONAL SAMPLES IN 1350° COLUMN USED TO SHOW EFFECT OF A FACTOR OPPOSING GRAIN GROWTH.									100% COARSE G.G.
1400°										100% G.G. FUSION

impact data (the figures give the foot-pounds of energy absorbed by the samples) and the occurrence and degree of abnormal grain growth. With a few exceptions, those samples affected by abnormal grain growth yielded low impact values. One exception was a sample showing only 30 per cent abnormal grain growth and having the high impact value of 63.5 foot-pounds, and another which was fine-grained and showing an impact number of 4.5 foot-pounds. Thus, it can be safely said that high speed steel possessed of abnormal grain growth is generally brittle, but this does not mean that all brittle high speed steel owes its brittleness to abnormal grain growth.

As expected, Table V very closely checks Table III for those heat treatments common to both. Since Table V represents the 14 per cent tungsten, 1 per cent vanadium, and Table III the 2 per cent vanadium steel, this is again indicative that vanadium has little effect on germinative temperatures, although it does somewhat tend to decrease the size of the abnormally large grains produced.

In Table V, also, the strain decreases for those treatments in which the straining temperature exceeds the hardening temperature. Thus the samples air-cooled from 1250 and 1300 degrees Cent. (2280 and 2370 degrees Fahr.) and hardened from 1200 degrees Cent. (2190 degrees Fahr.), and air-cooled from 1300 degrees Cent. (2370 degrees Fahr.) and hardened from 1250 degrees Cent.

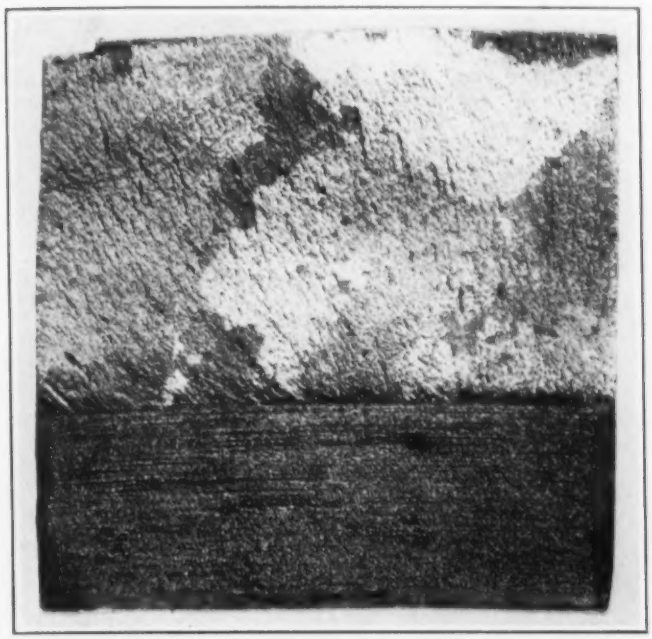


Fig. 4—Fracture of 14 Per Cent Tungsten Steel After 100 Hours at 1300 Degrees Cent. × 3½.

(2280 degrees Fahr.), show no abnormal grain growth. To check this once again, a sample was strained by air cooling from 1350 degrees Cent. (2460 degrees Fahr.), and hardened from 1300 degrees Cent. (2370 degrees Fahr.), and upon fracturing no abnormal grain growth was found. (Table V shows, also, this sample and two additional ones not shown in photograph in Fig. 3.)

The two additional samples were treated and fractured. One was air-strained from 1350 degrees Cent. (2460 degrees Fahr.), hardened from 1350 degrees Cent. (2460 degrees Fahr.), fractured, and exhibited 100 per cent grain growth. The other sample was strained from 1350 degrees Cent. (2460 degrees Fahr.) and hardened from 1400 degrees Cent. (2550 degrees Fahr.). When fractured it was found that fusion had occurred and therefore, as would be expected, no grain growth was found.

Homogenizing Treatment

Because of the heterogeneous character of high speed steel, it was thought possible that numerous sharp strain gradient systems would develop within a piece during cooling from elevated temperatures. Accordingly, an homogenizing treatment was attempted which

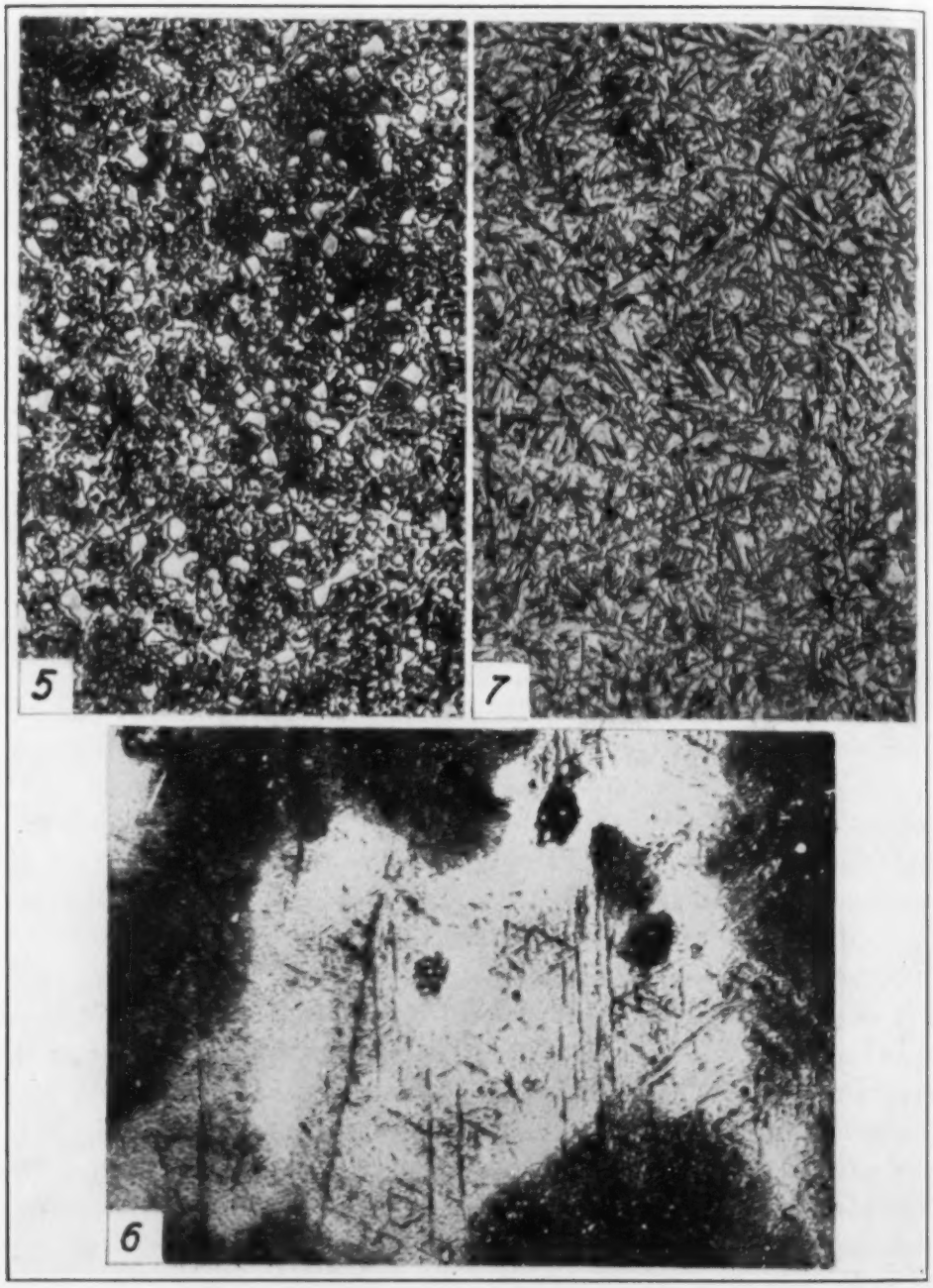


Fig. 5—Structure of the Steel Shown in Fig. 4 After a 3 Hour Anneal at 850 Degrees Cent. Etched with Nital. × 500.

Fig. 6—14 Per Cent Tungsten Steel, Annealed at 850 Degrees Cent., Following the Production of Abnormal Grain Growth. Etched with Nital. × 500.

Fig. 7—14 Per Cent Tungsten Steel Quenched from 1275 Degrees Cent., Following the 100 Hour Homogenizing Treatment. Etched with Nital. × 500.

consisted in heating one-half inch square pieces in evacuated quartz tubes at a temperature of 1300 degrees Cent. (2370 degrees Fahr.) for one hundred hours.

Fig. 4 shows the fracture of the steel immediately after the long treatment. The grains are the largest which were developed by any treatment, but this is considered normal due to the high temperature and length of time. After annealing at 850 degrees Cent. (1560 degrees Fahr.) for three hours the fracture appeared normal and the microstructure shown in Fig. 5 is considered quite uniform. For comparison the annealed structure of steel in which abnormal grain growth had occurred is shown in Fig. 6.

This material was then forged to three-eighths inch square, again thoroughly annealed at 850 degrees Cent. (1560 degrees Fahr.), and submitted to treatments which had usually produced abnormal grain growth. The steel was air-cooled from 900 degrees Cent. (1650 degrees Fahr.) and then heated quickly to 1275 degrees Cent. (2325 degrees Fahr.). Upon fracturing, the fracture was normally coarse, but could not be considered to have resulted from abnormal growth. An annealed piece was quenched from 1275 degrees Cent. (2325 degrees Fahr.) and fractured. A comparison showed no material difference in grain size. Upon requenching this last sample twice from 1275 degrees Cent. (2325 degrees Fahr.), but slight additional coarsening was noticed which can be accounted for by the longer exposure to the high temperature. The microstructure of the steel quenched once from 1275 degrees Cent. without drawing is shown in Fig. 7. This consists of well-developed martensite needles in an austenite matrix. It was noticed that in this condition the steel was much weaker, or strictly speaking, more brittle than the steel in its customarily hardened condition.

A Possible Explanation for the Mechanism of Thermal Strain Production

It is thought that, as a result of composition gradients in the steel, which have been so well discussed by Grossmann and Bain[3], small strain gradient systems may be induced upon cooling from above certain minimum temperatures. Fig. 6 shows the structural results of composition gradient, and shows also a considerable amount

[3]M. A. Grossmann and E. C. Bain, *Journal*, Iron and Steel Institute, 1924, No. 2, p. 249.

of austenite retained even after slow cooling (annealing). Depending upon the temperature from which the steel cools and the rate of cooling, more or less austenite will be present. With rapid cooling (air or faster) those portions low in alloy content will form more martensite and, because of the volume increase resulting from the austenite-martensite change, those portions rich in alloy which do not transform are considerably strained.

When the straining temperature exceeds 1200 degrees Cent. (2190 degrees Fahr.) it will be seen from Tables I and III, but especially No. 5, that the germinative temperature rises. This may seem anomalous but actually is in keeping with the idea that heterogenity is the cause of strain gradients. Beyond 1200 degrees Cent. (2190 degrees Fahr.) it is thought that more and more of the alloy-poor regions are retained austenitic, thus reducing the strains caused by martensitization, and with reduced strains a higher germinative temperature is required. The intensity of these strains is probably further influenced by the size of the piece, as previously suggested.

These ideas are supported by the total lack of abnormal grain growth in the steel which had been more or less homogenized. The structure of this material in the quenched condition (Fig. 7) is decidedly different from that usually found in quenched high speed steel and is undoubtedly the result of such a uniform composition that no portion of the steel is sufficiently high in alloy content to retain the steel in the fully austenitic condition for the cooling conditions given.

This steel in the quenched condition is entirely too brittle for use as a tool. It, therefore, appears that the value of high speed steel as used lies in its heterogeneous character.

Summary

(1) The so-called fish-scale or marble fracture is the result of abnormal grain growth.

(2) Strains of varying degree have been studied in relation to grain growth.

(3) As the strain apparently increases, the temperature at which large grains are formed decreases to a minimum at 1200 degrees Cent. (2190 degrees Fahr.) and no growth has been found at materially lower temperatures.

(4) As the straining temperature exceeds 1200 degrees Cent.

(2190 degrees Fahr.), the strain, instead of continuing to increase, decreases as indicated by a rise of the germinative temperature. Growth does not occur when the straining temperature exceeds the subsequent hardening temperature by more than 25 degrees Cent.

(5) The size of the sample seems to exert an influence on the degree of strain.

(6) Strains are probably the result of composition gradients as indicated by the fact that homogenized material would not produce the abnormal grain growth.

(7) The brittleness of the large-grained material is excessive without a material difference in hardness.

(8) The homogenized steel in the hardened state is also exceedingly brittle.

DISCUSSION

J. V. EMMONS:[1] Mr. Brophy and Mr. Harrington are to be congratulated upon their work which throws more light upon this interesting phenomenon in high speed steel. The publication of information such as this is a real service to the industry.

It has sometimes been observed that the size of the "marble" grains as measured on the fracture, is of a higher order of magnitude than the size of the austenitic grains as observed under the microscope. For instance, the "marble" grains may have an average diameter of 0.020 inch, while the austenitic grains may have an average diameter of 0.0005 inch. It has also been observed that many specimens of high speed steel having very large austenitic grains do not show a marble fracture. The reasons for this behavior have not as yet been definitely determined experimentally, but it is hoped that opportunity to do so will present itself at some future time.

A possible explanation which has suggested itself is that the cause of "marble" fractures does not lie so much in the size of the austenitic grains as in the development of their internal crystalline structure. The fracture in a hardened high speed steel does not usually take place along the grain boundaries but through the grains and preferably along a cleavage or slip plane. When the cleavage planes are suppressed or imperfectly developed, the fracture shows a matt appearance because the microscopic facets of the fracture are so differently oriented that the reflected light is thrown equally in all directions. When the favorable conditions, as shown in this paper, are present, the cleavage planes are believed to perfect their development in each grain and also to assume similar orientation in adjacent grains. A fracture passing through such a crystalline structure will at times be more or less parallel to the cleavage planes of a group of austenitic grains and will tend to follow these planes. Such a fracture will show patches of facets which all reflect the light in the same direction, forming the appearance which we call a "marble"

[1]Metallurgist, Cleveland Twist Drill Co., Cleveland.

fracture. If the reorientation of the cleavage planes in a group of austenitic grains progresses to the point where they become identical, then the grain boundaries disappear and the group becomes one grain of abnormal size.

A. H. d'ARCAMBAL:[2] We have read with considerable interest this excellent paper by Mr. Brophy and Mr. Harrington. It is indeed fortunate that the 18 per cent tungsten high speed steel rarely shows this fish scale fracture due to what the authors claim is abnormal grain growth. Quite often in order to obtain better machinability on a certain type of tool, we will take the rough machined blank, made from the 18 per cent tungsten steel, heat it in the neighborhood of 1600 to 1625 degrees Fahr., oil quench, and then finish machine. This blank will have a Rockwell hardness of over C40 after this treatment for machinability, but we do not obtain the fish scale fracture, even on the final product, though there is not an annealing operation between the heat treating and the hardening operation. In the case of the 14 per cent tungsten high speed steel, Mr. Brophy has shown that when a temperature around 900 degrees Cent. (1600 Fahr.) is used, and then quenched from the proper temperature this detrimental fish scale fracture results. We were also interested in the impact values shown by the authors. They have quite clearly proven that the unnotched specimens are more suitable for this work than the usual notched samples. However, impact tests on hardened high speed steel are at their best not entirely reliable. The authors obtain an impact reading of around 27 on specimens quenched from 1200 degrees Fahr., whereas specimens quenched from 1250 degrees Fahr. gave almost double this value. We should expect a higher value from specimens subjected to the lower heat.

In regard to the Rockwell hardness, it is interesting to note that apparently the 14 per cent tungsten high speed steel does not give as high an initial Rockwell hardness as the 18 per cent tungsten steel.

We trust the authors will continue their work along these lines, for it is quite evident that the presence of this fish scale fracture produces tools that give very short service.

S. L. HOYT:[3] I have had some interest in the past in the nature of high speed steel and it is on that account largely that this paper fascinates me because I believe that the authors have really brought into question the present conceptions of the nature of high speed steel. It is recorded here that the tempering treatment below the critical point has very little effect on the Rockwell hardness number. Mr. Brophy did not comment on this in presenting the paper. His comment was to the effect that a steel which shows fish scale structure has approximately the same Rockwell hardness as a steel which does not show the fish scale structure. But it is also true that tempering these steels had little or no effect on the Rockwell hardness. The point that I have in mind here is that presumably the authors selected this tempering temperature with the idea that if any austenite were present in the steel it would be converted into martensite and that therefore a difference in Rockwell hardness number should be brought out. If I am mistaken in that assumption, I know

[2]Manager of Small Tool Sales and consulting metallurgist, Pratt and Whitney Co., Hartford, Conn.

[3]Connected with the research laboratories, A. O. Smith Corporation, Milwaukee, Wis.

Mr. Brophy will correct me. With that in mind, to me it is surprising that the Rockwell hardness number shows no change for presumably the abnormal grain growth is due to strains set up in the first quenching or to a partial conversion of the austenite into martensite during quenching. Does it not also follow that the tempering treatment used should produce a definite change in the Rockwell hardness number?

I happen to know from previous discussions with the authors on this extremely interesting investigation that they do have other work in mind and I am sure we may await their additional information with a great amount of interest.

To me one of the most interesting parts of the paper is that on the "homogenized" sample in which it is shown that high speed steel owes some of its important properties to its heterogeneous character or to "persistent segregation," as Professor Sauveur would put it.

Authors' Closure

Reference to Tables I, III, and, particularly, Table V, shows that when the straining temperature, for the air-cooled samples, exceeds the succeeding hardening temperature by 50 degrees Cent. or more, abnormal grain growth does not occur during the hardening.

Air-cooling from the higher temperatures tends to retain more of the hardener in solid solution. Thus heating to 1350 degrees Cent. will dissolve a certain amount of the hardener (tungstides and carbides?). Most of this seems to be retained in solution by the air-cooling. Upon reheating to a hardening temperature of 1300 degrees Cent., some of the hardener may be precipitated as this temperature is 50 degrees Cent. lower than the previous solution temperature. This factor might tend to oppose grain growth during the heating at the lower hardening temperature.

The samples, that were strained by water cooling from the straining temperatures previous to hardening treatments, do not show this reversal. It seems possible that the greater strains of water-quenching may overcome the effect of a dispersed precipitate that, under other conditions, effectively opposes abnormal grain growth.

The writer feels that, although it appears difficult at this time to secure any definite proof for this explanation, the indicated precipitation should not be overlooked as a possible factor contributing to a surprising reversal in grain growth tendencies.

We wish to thank the gentlemen who have taken the time to study the paper and prepare discussions.

The question of grain size which Mr. Emmons discusses is interesting. It has been our experience, however, that the grain size as indicated by the fracture is the same as that seen under the microscope.

Mr. d'Arcambal reports that the 18 per cent tungsten steel rarely exhibits abnormal grain growth. This is due to the fact that the necessary straining temperature for this steel is much higher than for the 14 per cent tungsten steel. A series of samples of 18 per cent tungsten steel were put through the same program of treatments and abnormal grains developed at 1300 degrees Cent. for

straining treatments between 1150 and 1250 degrees Cent. and at 1350 degrees Cent. for straining treatments from 1000 to 1300 degrees Cent. As with the 14 per cent tungsten steel a limiting temperature below which no growth occurred was found but now the temperature was considerably higher. Also, as the straining temperature materially exceeded the second heating (hardening temperature) no growth occurred.

The difference in growing temperature may possibly be due to the presence of a larger quantity of hardener, which would tend to act as an inhibitor, and which would require a higher temperature for complete solution.

As Dr. Hoyt states, additional work is in progress and we wish to reserve the right to change our opinions as to the causes of this phenomenon. It is our object to throw additional light on the nature of these interesting alloys.

SOME NEW ASPECTS OF THE IRON-CARBON DIAGRAM

By H. A. Schwartz

Abstract

The purpose of the paper is to awaken interest in the viewpoint that the equilibrium diagram is the expression of definite energy relations and not merely a plot of certain observed transformation points.

As an illustration of this viewpoint the A_{cm} and A_{gr} lines are studied in the light of the solubility equations and of the known specific heats of iron, carbon and cementite.

Conclusions are drawn as to the metastability of free cementite at all temperatures above that at which the work done in expansion restrains the graphitizing reaction.

No such temperature has been demonstrated to exist but its possibility is indicated. Evidence is offered in support of the fact that the solid solutions of the stable and metastable systems differ in kind.

Graphitization is demonstrated in two unusually pure iron-carbon alloys.

THE iron-carbon equilibria have been studied at such length that it may seem that nothing new can be said on the subject. It appears, however, that although many able investigators have refined the observational methods and improved the precision of its experimental basis, only Cesaro,[1] has attempted an interpretation of any portion of the diagram on the basis of chemical thermodynamics. Since this is written, Yap, Chu-Phay[2] has contributed two papers, in the same field and confirming in part Cesaro's conclusion.

The writer has also since found a discussion of the equilibrium curves of the system iron and carbon by von Jüptner, *Iron and Steel Magazine,* Vol. XI, p. 377, 1906, which is entitled to mention.

[1]Cesaro, "Note on the Liquidus in the Iron-Carbon Diagram," *Journal,* Iron and Steel Institute, Vol. XCIX, p. 447.

[2]Yap, Chu-Phay, "A Thermodynamic Study of the Phasial Equilibria in the System Iron-Carbon."

"Influence of Dissolved Carbide on the Equilibria of the System Iron-Carbon," Technical Papers Nos. 381 and 382, American Institute of Mining and Metallurgical Engineers.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, H. A. Schwartz, is a member of the society. He is manager of research, National Malleable and Steel Castings Co., Cleveland. Manuscript received April 28, 1931.

Believing that most problems, notably the identity or lack thereof of the stable and metastable solid solutions, the mechanism of graphitization during freezing, the possible stability of Fe_3C at low temperatures and the existence of molecules in crystalline solids, in the sense of a unit of subdivision, between a crystallite and an atom in size, are unlikely to be soon solved by further refinements of observation but can be settled readily in the light of available energy data, the present study was undertaken.

Only a limited amount of new experimentation was required but it is believed that in dealing with the low temperature graphitization of a pure iron-carbon alloy we were able through the kind cooperation of our friends to exclude the effect of other elements more perfectly than our predecessors in the field.

The so-called double diagram is now so generally accepted among American and Continental metallurgists that a further defense of this method of representation of the equilibrium conditions in iron-carbon alloys may be dispensed with.

The assertion that metastable equilibrium is by its very definition not a true equilibrium diagram is no doubt correct in strict logic, but the interpretation of two superimposed diagrams is so generally understood that this objection has little practical validity. It is the writer's purpose to deal with the viewpoint that graphitization involves a ternary system.[3]

Range of Metastability of Fe_3C

The question whether there is a minimum temperature for the metastability of Fe_3C is incapable of direct experimental answer. The writer has referred elsewhere[4] to the fact that centuries would be required to precipitate measurable amounts of graphite at room temperature under usual quantitative time-temperature-graphite relations.[5,6,7]

[3]Hanson, "The Constitution of Silicon-Carbon-Iron Alloys and a New Theory of the Cast Irons," *Journal,* Iron and Steel Institute, Vol. CXVI, No. II, p. 12.

Kotaro Honda, "On Graphitization of Iron-Carbon Alloys," *Journal,* Iron and Steel Institute, Vol. CII, No. II, 1920, p. 287.

[4]"Quelques Theories de Graphitization," Bulletin de l'Association Technique de Fonderie, Sept. 1928, p. 279.

[5] Schwartz, "Graphitization at Constant Temperature," Transactions, American Society for Steel Treating, Vol. 9, p. 883 and Vol. 10, p. 53.

[6]Schwartz, "Graphitization at Constant Temperature below the Critical Point," Transactions, American Society for Steel Treating, Vol. 10, p. 965.

[7]Schwartz, "The Mathematics of Graphitization below the Solidus," Paper No. 62, World's Engineering Congress, Tokio, Japan.

Within the lifetime of several generations of observers we would not, therefore, be able to decide whether graphitization is inhibited at room temperature or merely enormously retarded in rate. We may approach the matter indirectly from the principle that reactions proceed spontaneously in that direction which reduces the energy content of the system.

All recent investigators agree that cementite is endothermic although there is difference of opinion as to the amount of heat liberated by its decomposition.

Ruff,[8] Brodie, Jennings and Hayes,[9] Maxwell and Hayes[10] and perhaps others, assign a value of the order of magnitude of —14,000 cal/mol for the heat of formation, while Watase[11] and Roth[12] offer a value of the order of magnitude of —4,000 cal/mol. Unfortunately it is necessary, as will be shown shortly, to decide between these groups of values in order to answer our question. The data are all presumably at constant pressure and the calorimetric values, i.e., all except Maxwell's, are at approximately room temperature.

The physical chemist uses an expression for the change in energy content of a system for a reaction at constant pressure

$$\triangle U = \triangle H + p\,dv = \triangle H + W$$

i. e. the change in energy content, $\triangle U$, is made up of the change in heat content, $\triangle H$, and the work, W, done by the system against the external pressure, p, by its change of volume, dv. Where pressure, p, is not too great and the change of volume accompanying the reaction is small, which latter is usually true of solids, the p dv term may be negligible.

During the decomposition of Fe_3C there is an increase of volume since carbon and iron, in the proportion to form cementite, occupy

[8]Ruff, "The Metallography and Heat Treatment of Iron and Steel," Sauveur, p. 449.

[9]Brodie, Jennings and Hayes, "Heat of Formation of Cementite as Electrolyzed from a Pure Iron-Carbon Alloy of Eutectoid Structure and Composition," TRANSACTIONS, American Society for Steel Treating, Vol. X, No. 4, p. 615.

[10]Maxwell and Hayes, "The Free Energy and Heat Formation of Iron Carbide for the Temperature 650 Degrees to 700 Degrees," *Journal*, American Chemical Society, April 1926, Vol. 48, p. 584.

[11]Watase, "The Heat of Formation of Cementite," Science Reports of the Tohoku Imperial University, Series I, Vol. XVII, No. 6, p. 1091, September 1928.

[12]Roth, "Beitrage zur Thermochemie des Eisens, Mangans und Nickels," Archiv fur das Eisenhuttenwesen, Vol. 3, No. 5, Nov. 1929, p. 339.

a greater volume than does the compound. This increase of volume is accomplished by stretching the iron and hence does work. Graphitization will only proceed if the energy required to do this work is less than that liberated by the decomposition of Fe_3C.

The density of Fe_3C has been variously determined as between 7.39 and 7.66. For our purpose we may accept a value of 7.45. The density of graphite in iron has been determined as being from 2.48 to 2.51, say 2.50, and the density of alpha iron is very close to 7.89.

If 180 grams of cementite decompose into 12 grams of carbon and 168 grams of iron, the resulting increase in volume will be

$$\frac{12}{2.5} + \frac{168}{7.89} - \frac{180}{7.45} = 4.8 + 21.3 - 24.2 = 1.9 \text{ cc}$$

which is a cubic expansion of about 8 per cent. This is equivalent to a linear expansion of .02 2/3. The modulus of elasticity being 29,000,000 pounds per square inch = say 2,000,000 kilograms per square centimeter, the work done in expanding the cubic centimeter of metal will be roughly

$$3 \times .02^{2}/_{3} \times \frac{2{,}000{,}000 \times .02^{2}/_{3}}{2}$$
$$= 2132 \text{ kilogram centimeters}$$
$$= 21.32 \text{ kilogram meters}$$

Using Brodie, Jennings and Hayes' figure,

$$\text{Heat of formation of 1 cc } Fe_3C = \frac{13600 \times 7.45}{180}$$
$$= -452 \text{ calories}$$
$$= -105.9 \text{ kilogram meters.}$$

There is thus, even at room temperature, about five times as much energy available by the decomposition of cementite as is required to do the mechanical work of dilating the metal. Using the lower values there is still a surplus according to Watase or Roth.

The only probable source of error is our lack of knowledge of the coefficient of elasticity for cubic expansion. If this be far out of line with Young's modulus, an error exists.

The coefficient of compressibility[13] of any metal is

$$E_v = \frac{E}{3\ (1 - 2\ r)}$$

in which for iron,

$$E = 29{,}000{,}000$$

and

$$r = 0.30$$

This yields a value of about 24,000,000.

If this bulk modulus be the same in compression and tension, the force which would produce a change of volume of 8 per cent would be 1,920,000 pounds per square inch = 132,000 kilograms per centimeter as against 970,000 pounds per square inch from the previous calculation, and the work done, calculated as before, becomes 52.8 kilogram meters per cubic centimeter. The reaction can proceed if the larger numerical value of heat of formation is correct, but not if the lower one is substantiated. Hence mechanical conditions possibly restrain graphitization near room temperature.

It is, of course, obvious that a similar calculation, using the physical constants at other temperatures, could be carried through to determine whether or not cementite may graphitize. Alternatively, if sufficient data are at hand, the various densities, the heat of formation and the modulus of elasticity might be expressed as functions of temperature and from these the difference between heat of formation and mechanical work be written in an equation in terms of temperature. We know that the modulus of elasticity is nearly constant from somewhat below to somewhat above room temperature and usually decreases by some 33 1/3 per cent by the time a temperature of about 1000 degrees Fahr. (1830 degrees Fahr.) is reached,[14] the reaction should then proceed even if the numerically lower heats of formation are accepted. At this temperature a good deal of viscous flow, or creep, goes on and a rather small constant force will produce any amount of deformation given sufficient time. This viscous flow becomes more pronounced the higher the temperature

[13] Jeffries and Archer, "The Science of Metals," p. 13.

[14] H. J. French and W. A. Tucker, "Available Data on the Properties of Irons and Steels at Various Temperatures," *Transactions* of the American Society of Mechanical Engineers, 1924, Vol. 46, p. 97.

and the work term will change with reaction velocity. When the force thus becomes dependent on rate of deformation, the mechanical work term may fix the possible limit of graphitizing rate. Umino[15] has shown that the specific heat of cementite is greater than that of its constituent elements. Hence the heat of formation of Fe_3C decreases, algebraically, with temperature.

Since, therefore, the heat evolved by the decomposition of cementite increases with temperature and the mechanical constraint decreases, the once possible reaction can not terminate for mechanical reasons at higher temperatures. Whether a termination at low temperatures exists is not known until we are assured of the true value of E_v in tension and of the heat of formation. A lower limit is at least possible.

Having thus determined that there is possibly a lower limit of temperature for the metastability of cementite within the range for which we possess data, let us examine the question of an upper limit.

If the mean specific heat of a compound differs from the average mean specific heat of its components, the heat of formation will be a function of temperature.

The principle of the conservation of energy will require that heat of formation of a compound at a given (lower) temperature (T_1), plus the heat required to raise the compound to a (higher) temperature (T_2), must equal the heat required to raise the components from T_1 to T_2, plus the heat of formation at T_2. Let us examine what effect the difference of specific heats of Fe_3C and Fe + C has on the heat of formation of Fe_3C at elevated temperatures and particularly whether the heat of formation may ever become zero or positive.

The data of Umino (loc. cit.), although pointing in general to a higher mean specific heat of Fe_3C than of the mixture of elements, are perhaps rather difficult of interpretation in the high temperature ranges. His individual determinations of mean specific heat in the interval from 900 to 1100 degrees Cent. (1650 to 2010 degrees Fahr.) inclusive are sufficiently concordant to point to a probable error of a single observation of specific heat of about 0.0002 or about 0.00012 in the reported values which are usually the average of three determinations. This means that his observations of sensible heat

[15]Umino, "On the Specific Heat of Carbon Steels," *Science Reports* of the Tohoku Imperial University, Vol. XV, No. 3, 1926, p. 354.

must have been reproduced to about 0.1 calories per gram.

However, a plot of the total heat content per gram of metal containing 1.41, 1.57 and 2.84 per cent total carbon shows an arrangement much more variable than consistent with such precision. His own Fig. 5 can scarcely be interpreted to mean anything more than that the sensible heat at a given temperature is substantially independent of carbon content, if above 1.40 per cent at all temperatures from 100 to 1250 degrees Cent. (210 to 2280 degrees Fahr.) The writer ventures to point with surprise to the fact that although the heat content increases, with carbon (from 1.57 to 2.84 per cent) for temperatures from 850 to 1100 degrees Cent. (1560 to 2010 degrees Fahr.) inclusive, where both alloys were solid, it does not increase with carbon at 1200 and 1250 degrees Cent. (2190 to 2280 degrees Fahr.) where the high carbon iron would have contained not only sensible heat but also the latent heat of fusion of its ledeburite.

Umino did not choose to compute the specific heat of cementite above 900 degrees Cent. (1650 degrees Fahr.) Several means are available for approximating the specific heat at higher temperatures. For example, we may, up to the eutectic temperature, consider his 2.84 per cent carbon alloy a mixture of 1.75 per cent carbon steel, (a little above saturated austenite at 1130 degrees Cent.) and cementite.

We may extrapolate from his data for the three steels of 1.235 per cent carbon, 1.41 per cent carbon and 1.575 per cent carbon steel. The extrapolation will be reliable precisely to the extent that his series of investigations are strictly comparable.

Umino's data and the graphically extrapolated value for 1.75 per cent carbon steel are shown in Table I.

Table I

	Calories per gram Determined by Umino			Extrapolated
Carbon	1.235	1.41	1.575	1.75
900°C.	144.0	144.0	146.6	147.5
1000°C.	157.9	156.1	160.0	160.0
1100°C.	174.9	173.1	172.0	170.8
1200°C.	190.0	189.0	187.0*	186.1*
1250°C.	199.0*	197.0*	195.3*	193.8*

*partially molten.

Since 2.84 per cent carbon metal is $\frac{109}{492}$ Fe_3C and $\frac{383}{492}$, 1.75 per cent carbon steel, we may from Umino's determinations on that

Table II

	Calories per gram		
	Extrapolated	Umino's Determination	Calculated Fe_3C
Carbon	1.75	2.84	.....
900°C.	147.5	148.2	150.7
1000°C.	160.0	164.4	179.9
1100°C.	170.8	175.0	207.2
1200°C.	190.0	187.0	190.0*
1250°C.	199.0	192.5	187.9*

*These figures were obtained by the use of data at temperatures where the alloys are partially molten.

metal and our extrapolated values calculate the heat content of cementite. (Table II.)

In case of semi-molten alloys, Umino's measured total heat would include the latent heat of fusion of a portion of the alloy, this amount increasing with the temperature and carbon content. It would, therefore, appear that as a result the calculated heat content of cementite would be larger than the true value, not smaller as they appear to be in the column of Table II.

By extrapolation from the first three members in the last column of Table II a heat content of 232.5 calories per gram is indicated for cementite at 1200 degrees Cent. (2190 degrees Fahr.) and one of about 249 calories at 1250 degrees Cent. (2280 degrees Fahr.)

We may further evaluate Umino's data by computing from his data at and below 900 degrees Cent. (1650 degrees Fahr.) an expression relating heat content to temperature and by means of such an equation extrapolate above 900 degrees Cent. Such an equation has been calculated by least squares, by H. H. Johnson, from Umino's original data.

Table III

		Calories per gram of Fe_3C
	100	14.8
	200	29.7
Umino's	300	44.7
	400	60.2
Values	500	76.2
	600	93.4
	700	111.9
	800	131.9
	900	153.9
	1000	179.0
Extrapolated	1100	204.4
	1200	233.2
	1300	264.8

In Table III the data up to 900 degrees Cent. are Umino's values, those above are calculated from the equation

$$\text{Total calories} = -1.295 + 6.0843\ T - 0.46778\ T^2 + 0.07609\ T^3 - 0.00109\ T^4$$

Attention is invited to the fact that this extrapolation agrees well with the extrapolation from Table II.

Schmidt[16] finds the total heat of the solid eutectic at the melting point to be 200.8 calories. From the values for cementite in Table III and for 1.75 per cent carbon metal in Table I, a value of about 193 would be interpolated which is at least rough corroboration.

From Umino's Fig. 10 and tabular matter we may obtain the heat content per gram of a mixture of the constituents of cementite, iron and carbon, by multiplying his mean specific heats by the temperature and can compare these with the heat contents of Fe_3C from our Table III.

Table IV

Temp. Degrees Cent.	3 Fe + C Mean Specific Heat after Umino	Calc. Capacity	Fe_3C Umino and Extrapolated	Difference
100	0.1161	11.6	14.8	3.2
200	0.1212	24.2	29.7	5.5
300	0.1254	37.6	44.7	7.1
400	0.1319	52.8	60.2	11.4
500	0.1381	69.0	76.2	7.2
600	0.1465	87.9	93.4	5.5
700	0.1543	108.0	111.9	3.9
800	0.1691	135.3	131.9	−4.4
900	0.1828	164.5	153.9	−10.6
1000	0.1833	183.3	179.0	−4.3
1100	0.1837	202.1	204.4	+2.3
1200	0.1844	221.3	233.2	+21.9
1300	0.1849	240.4	264.8	+23.4

It will be seen that, except for the perturbation in the critical range, the heat content of Fe_3C is always greater than that of 3 Fe + C, hence the heat of formation of Fe_3C decreases (algebraically) with temperature, with the exception noted. Being already negative, this means a numerical increase of a negative number with rising temperature and hence greater instability. Umino's data, therefore, contradict the existence of any high temperature field in which Fe_3C might be stable toward graphite.

It appears that the decreasing values after the first three, in the

[16] Schmidt, "Spezifische und Erstarrungs-Warme des geschmolzenen Roheisens," *Metallurgie* I, 1910, p. 164.

last column of Table II, representing as they do a physical impossibility, are to be explained, from their method of derivation, by an abnormally low heat content in Umino's 2.84 per cent carbon alloy at the corresponding temperature. Umino thus recovered less than the heat content computed from Fe_3C and steel and more than that computed as a mixture of steel and carbon. His results might then be considered consistent with a partial graphitization at the time of quenching. We have no better explanation for the discrepancy.

Cementite is thus theoretically metastable toward carbon at all temperatures above the eutectic melting point. This fact should especially be kept in mind as it will later be used in establishing other conclusions regarding the nature of hypereutectic alloys.

Graphitization in Pure Binary Alloys

Several writers, including the present author, have reported instances of apparent absence of graphitization in fairly pure white cast irons. Reference has already been made to Honda and Murakami, Hanson and Norberry, who have studied the graphitizing reaction from the viewpoint of other elements. It appeared important therefore, to furnish, if possible, experimental verification of the fact of graphitization in the purest available alloy.

It was desired to answer the following questions:

> Will metal free from silicon graphitize, especially below the critical point?
>
> Will metal graphitize without the presence of CO and CO_2? More generally, is graphitization a phenomenon in which other elements than iron and carbon participate?

Experimentally this required that we heat treat the purest possible iron-carbon alloy of high carbon content in the highest convenient vacuum for a fairly long time to a temperature somewhat below A_1 and determine whether or not there is a decrease of "combined" carbon content.

Two alloys were made for us by the Bureau of Standards in the apparatus used for the determination of gases in iron in Jordan's laboratory. It is assumed that the resulting melts would be free from gases in analytically detectable amounts. Concerning the preparation of these samples the Bureau writes in part as follows:

"We are also sending you enclosed with this letter a small piece of iron-carbon alloy representing the entire cross section of a melt of rather pure iron (either Armco iron or electrolytic iron) made in an Acheson graphite crucible in our vacuum fusion gas analysis equipment. This sample was held molten at approximately 1550 degrees Cent. (2820 degrees Fahr.) under a vacuum for about half an hour. By that time, the total pressure of gas (almost entirely CO) over the liquid metal was of the order of 0.01 millimeter of mercury. The furnace current was then cut off. We have no record of the time then required to cool but we estimate that the metal froze within one or two minutes and cooled to below a visible heat in possibly fifteen minutes. The total carbon in this specimen is probably close to 5.0 per cent. Possibly an examination of this sample will be of interest to you.

Respectfully,
(Signed) George K. Burgess, Director.

Enclosure:
Sample iron-carbon alloy."

"We have been glad to prepare for your use two small additional melts made under conditions very nearly the same as those described in paragraph 3 of our letter of September 19th. The only difference in the preparation of the two present samples is that these samples were held molten for about 1 hour at 1500°C. and the pressure at the end of the heating period was of the order of 0.1 mm. of mercury. The sample marked "A" was prepared by melting Armco iron in graphite and that marked "E" by melting electrolytic iron. We are mailing these samples to you under separate cover.

Respectfully,
(Signed) L. J. Briggs, Acting Director,
George K. Burgess, Director.

Separate Cover:
Two iron-carbon alloys."

Through the courtesy of Mr. W. P. Sykes, the National Lamp Works of the General Electric Company sealed portions of these melts into hard glass tubes at a pressure of probably less than one micron. Mr. G. M. Guiler sealed these tubes, packed in asbestos wool into a quartz bulb, evacuated this to a pressure of a few millimeters of mercury column and sealed it. The purpose of the quartz container was merely protection to the delicate glass bulbs. The tube was heated in a portion of a Dressler continuous kiln whose temper-

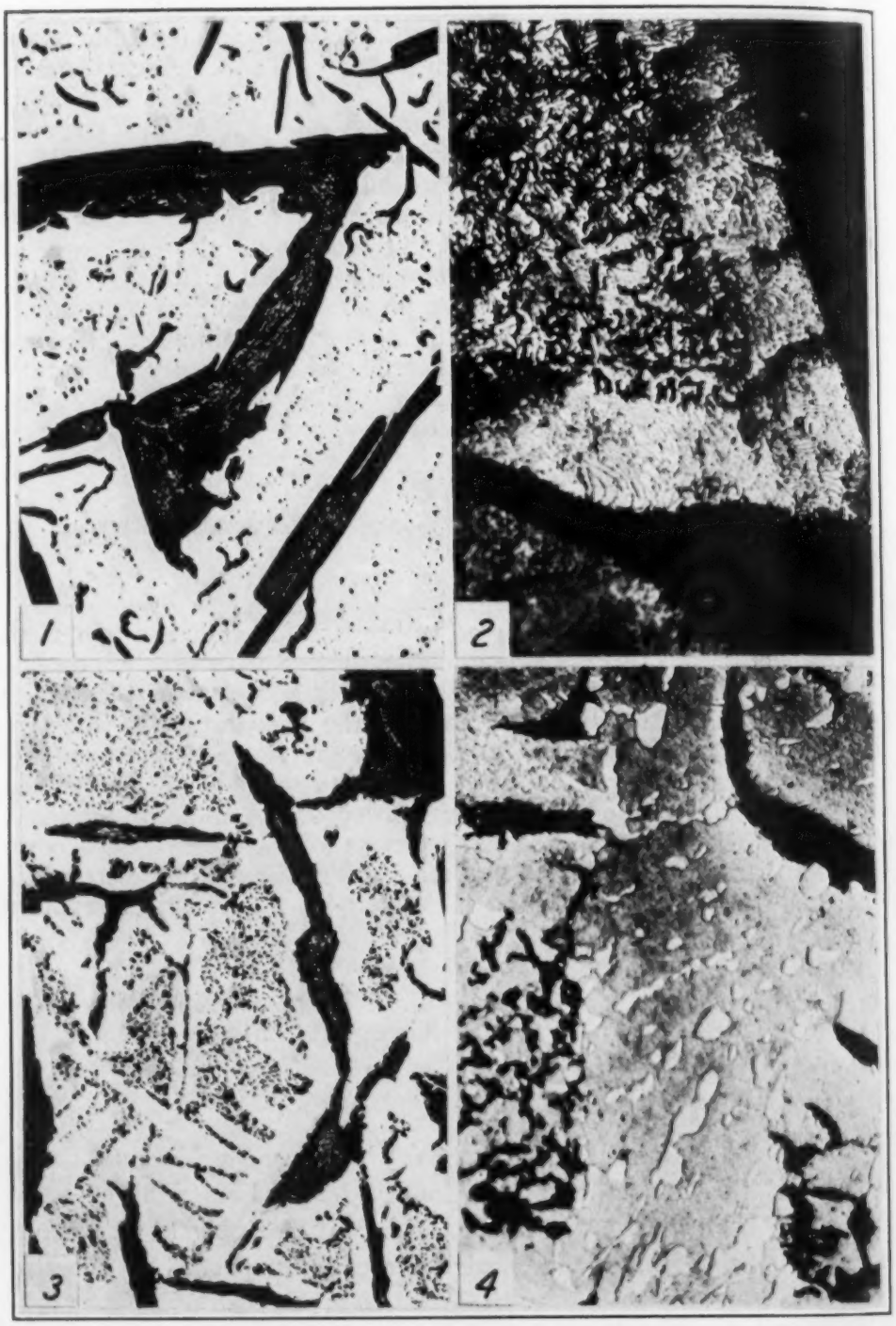


Fig. 1—Armco Iron, as cast. Unetched. × 100.
Fig. 2—Armco Iron, as cast. Nitric Acid Etch. × 500.
Fig. 3—Armco Iron, annealed. Unetched. × 100.
Fig. 4—Armco Iron, annealed. Nitric Acid Etch. × 500.

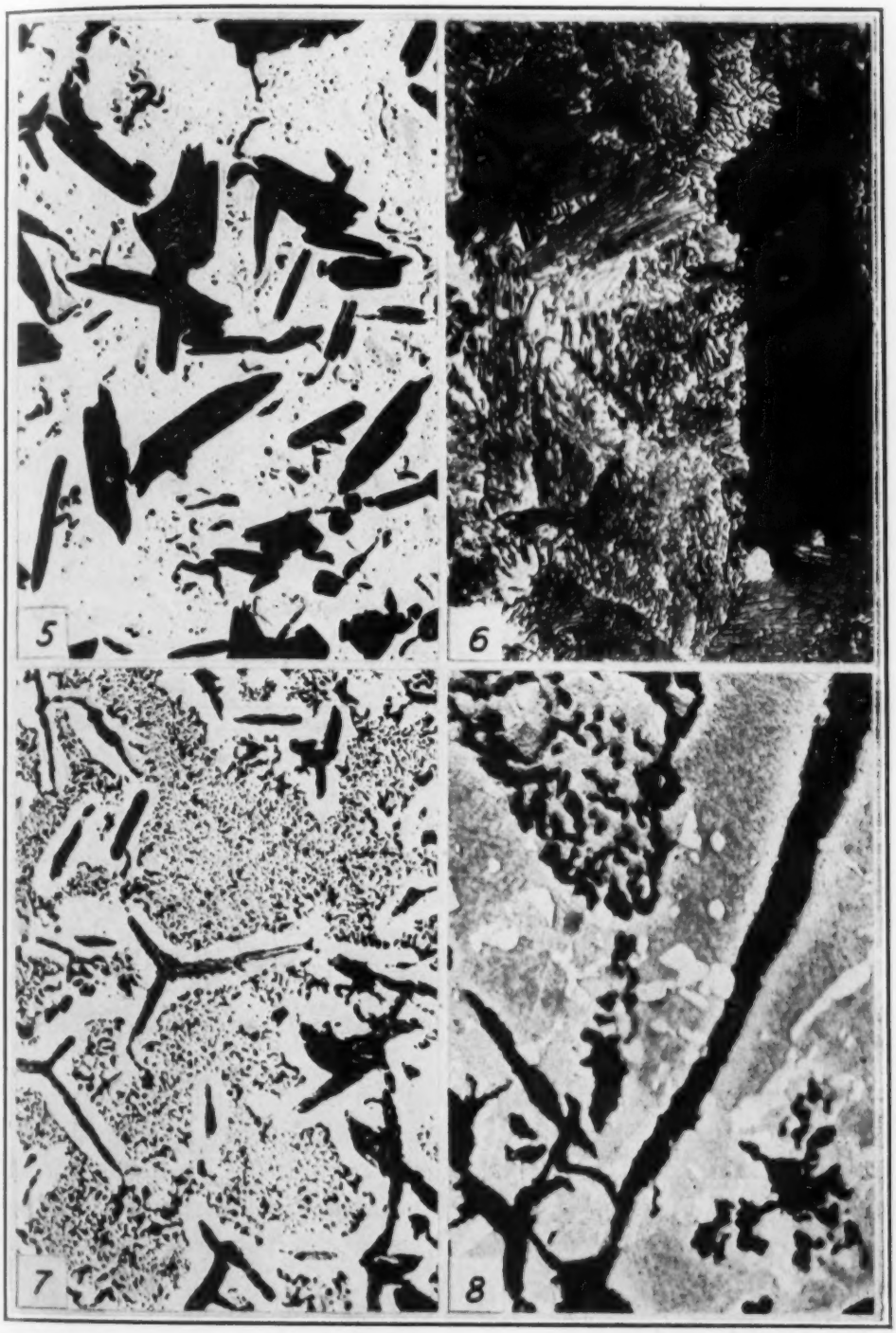


Fig. 5—Electrolytic Iron, as cast. Unetched. × 100.
Fig. 6—Electrolytic Iron, as cast. Nitric Acid Etch. × 500.
Fig. 7—Electrolytic Iron, annealed. Unetched. × 100.
Fig. 8—Electrolytic Iron, annealed. Nitric Acid Etch. × 500.

ature varied slowly between the approximate limits, 600 and 650 degrees Cent. (1110 and 1200 degrees Fahr.) for about 2000 hours.

On opening the quartz tube the glass tubes were found sound but collapsed tightly on to the iron specimens under the slight pressure in the quartz tube which is evidence against the expulsion of any gas on heating. The glass was a deep brownish black and could be readily removed from the iron. On solution in HF and H_2SO_4 the discolored glass left traces of a dark powder which may or may not have been free carbon.

Photomicrographs of the specimens by C. H. Junge before and after heat treating are shown in Figs. 1-8 inclusive.

The distribution of graphite and combined carbon is in each case somewhat nonuniform so that sampling for carbon determinations presented some difficulty. It was executed best by dissolving average cross sections of the specimens as single pieces in nitric acid or double copper chlorides accordingly as graphite or total carbon was required. The analyses resulted as follows:

Table V

	Made from			
	Armco		Electrolytic Iron	
	As Cast	Heat Treated	As Cast	Heat Treated
Total Carbon	7.48	6.35	7.47	5.61
Graphite	6.60	5.59	6.60	5.32
Combined Carbon by diff.	0.88	0.76	0.87	0.29
Combined Carbon by color	0.90	0.77	0.87	0.30
Mn	0.020	0.020	none	none
Si	0.009	.....	0.029	....
P	0.002	.....	0.015	....
S	0.020	.....	0.007	....
Total impurity	0.051	.....	0.051	....

The values pertaining to carbon are averages of concordant duplicate determinations or more.

It appears that even in these very pure binary alloys graphitization occurs during freezing and proceeds below A_1 though slowly. It appears also that carbon will leave such metal at low external pressure. It is thus shown that graphitization is a phenomenon to be found in metal which consists of over 99.94 per cent iron-carbon alloy.

The microscopic appearance of the samples as made in the melting furnace furnishes unmistakable evidence of the formation of graphite at temperatures very near to, if not above, the eutectic melting point. Further proof of high temperature graphitization in the

melting furnace is furnished by the great amount of graphite precipitated in the very short time occupied in cooling. Either the graphite crystallized as such or, if derived from Fe_3C, the reaction was so tremendously rapid as to require extremely high temperatures.

The experimental conditions appear to exclude the presence of detectable amounts of gas during the melting, freezing or subsequent graphitization and hence to dispose of the Honda and Murakami view that the reaction

$$C + CO_2 = 2\ CO$$

forms an essential step in graphitization. There is, however, no intention of denying that it may accelerate the rate of reaction.[17]

It is to be pointed out that it would be incompatible with the second law of thermodynamics for Fe_3C to be oxidizable by a mixture of CO and CO_2 which would precipitate carbon unless Fe_3C is metastable toward carbon.

The experiment described above has a bearing on Hanson's work on ternary systems containing silicon for it is the limit at zero silicon of such a series of alloys as were studied by that worker. Hanson concludes from the additional degree of freedom allowed a ternary system, as compared with a binary by the presence of an extra component, that there may be fields in which three phases, C, Fe_3C, and either ferrite or austenite, may be in equilibrium with each other. His experimental data lead him to conclude that below A_1 ternary alloys of very low carbon are in equilibrium when consisting of Fe and Fe_3C; alloys of somewhat higher carbon contain all three phases and alloys of still higher carbon are Fe and C when in equilibrium. His diagrams show the boundaries between these three fields to shift in the direction of higher carbon with decreasing silicon. Hence, in the limit of silicon being zero, the Fe-Fe_3C and Fe-Fe_3C-C fields should be of maximum width.

Now first, the phase rule deals only with the character and number of phases in equilibrium and not with their relative amount.[18] Further, it assures us that a binary alloy can, at most, have two phases in equilibrium at a given series of temperatures and pressures.

[17]Hayes and Scott, "The Catalysis of the Graphitization of White Cast Iron by the Use of Carbon Monoxide-Carbon Dioxide Mixtures when Applied under Pressure," *Transactions*, American Foundrymen's Association, Vol. XXXIII, pp. 574-593.

[18]H. M. Howe, "The Metallography of Steel and Cast Iron," p. 33.

Second, our experiment has shown that a three-phase system, Fe-Fe_3C-C, at 650 degrees Cent. (1200 degrees Fahr.) reacts in the direction of the elimination of the Fe_3C even at 0.03 per cent silicon and 0.29 per cent agraphitic carbon. Hence it is safe to conclude that the binary system will, when in equilibrium, consist of iron and carbon (the slight solubility of carbon in alpha iron being recognized but neglected).

This conclusion contradicts that derived from Hanson's data by extrapolating them to their limiting values. The author, in a discussion of Hanson's original paper, has pointed to a possible source of error in that worker's experimentation and will not here enlarge further on the matter beyond pointing out that Hanson's data are not apparently reconcilable with ours.

Austenite and Boydenite

The author some years ago[19] suggested that the solid solution in equilibrium with Fe_3C austenite, is different in kind from that in equilibrium with carbon which we called Boydenite; later[20] we suggested in what this difference might consist.

It is known that the added carbon atom distends the lattice parameter of gamma iron and may be confidently assumed that a small carbon atom substituted for an iron atom as postulated for boydenite would cause a decrease in lattice parameter. Mechanical work is therefore done in causing a substituted carbon atom to take an additive position and boydenite should be stable toward austenite.

It is an accepted fact that the A_{gr} line marking the equilibrium of C and solid solution (boydenite) is less steep and to the left of the A_{cm} line marking the equilibrium of Fe_3C with austenite. If prolonged upward the two would intersect at a temperature above the eutectic melting point at which temperature carbon and Fe_3C would be in equilibrium with solid solutions of equal carbon concentration, i.e., with the same solution if boydenite does not differ in kind from austenite. Therefore at that temperature C and Fe_3C are also in equilibrium with each other, i.e., the heat of formation of Fe_3C is zero. But we have shown previously that the heat of formation rises, numerically, with increasing temperature and hence can not become

[19]Schwartz, "Conditions of Stable Equilibrium in Iron-Carbon Alloys," *Mining and Metallurgy*, August 1922.

[20]Schwartz, "Evidences Concerning the Location of the Carbon Atom in Boydenite," Transactions, American Society for Steel Treating, Vol. XI, p. 277.

zero in this temperature range. Hence C and Fe_3C are never in equilibrium at elevated temperatures and hence two solutions of equal concentration one in equilibrium with C, the other with Fe_3C, are not in equilibrium but differ in energy content and hence are not identical in kind. Being different in energy content a thermodynamic study based on the loci of the A_{cm} and A_{gr} lines cannot but be profitable.

Are Elements Monatomic in Solid Solution

It is known that, providing only the specific heat of a substance in the free state and in solution is the same, as it frequently is, if x is the molal concentration of a saturated solution at absolute temperature, T, then

$$\log x = \frac{A}{T} + B \qquad (1)$$

where A and B depend upon certain thermal constants of the excess substance. Leaving the significance of these constants for the present, let us turn to the use we can make of this equation in determining the molecular weight of the substance not present in excess.

Evidently for a given weight percentage concentration of a certain (solid) solution, the molar concentration will depend upon the relative numbers of atoms per molecule in the solute and solvent. If we know experimentally the relation of weight percentage concentration to temperature and can find some relation, n, of the number of atoms in a molecule of solvent and solute respectively which will cause the molal concentration to also satisfy equation (1), that value, n, or one of its multiples, will represent the number of atoms in a molecule of solvent.

Ruer and Iljin [21] have determined the solubility of carbon in the stable system for various temperatures and obtained the values shown in Table VI.

Table VI

T in C.°	Solubility in Per Cent Carbon
1120	1.25
1100	1.24
1000	0.99
900	0.84
800	0.75

[21] Ruer and Iljin, "Zur Kenntnis des stabilen Systems Eisen-Kohlenstoff", *Metallurgie*, Vol. VIII, Part 4, 1911, pp. 97-101.

These figures can be represented by the empiric equation deduced by the method of least squares

$$(C - 0.4706)\ (Y - 0.0006) = 0.002023 \qquad (2)$$

where C is carbon concentration in per cent by weight and Y is the reciprocal of the absolute temperature in degrees Cent. The relation is purely empiric, but the individual determinations agree with the equation within a probable error of 0.0036 per cent carbon, which is probably considerably better than the precision of observation.

Now it is shown in Appendix A that equation (1) can be made identical with an equation

$$(C + a)\ (Y + b) = K \qquad (3)$$

which is of the form of (2) if $K = O$, as is not here the case, (i.e. if either C or Y are constant). Or the two forms can be made identical if $n = \pm \infty$. The value $-\infty$ is meaningless and the value ∞ is nearly so, for then x is also infinite and besides no finite mass of atoms can contain an infinite number.

It then appears that mathematically we can not compute the desired number, n, for equations (1) and (2) are incompatible. We do not, however, require mathematical identity for our equation but only an agreement with a precision beyond that of our observations.

T. M. Chapman calculated, by the method of least squares, for various values of n, the constants A and B in equation (1) which would produce the best agreement with the observational data and then calculated the probable error of a single reading as compared with the equation. The results are as follows:

Table VII

n	A	B	P. E. Per Cent Carbon
0.125	−1091	−2.641	0.028
0.25	−1084	−2.193	0.028
0.50	−1072	−1.220	0.026
1.0	−1049	−1.493	0.028
2.0	−1005	−1.739	0.024
4.0	− 926	−1.940	0.022
25.0	− 512	0.140	0.029
50.0	− 334	0.112	0.007
100.0	− 198	0.074	0.006
1000.0	− 24	0.010	0.0000+

We do not find in the Ruer and Iljin reference any information

as to the precision of a single recorded point. If we assume a probable error of 0.01 per cent carbon, arbitrarily, which is not higher than we would expect in very good work of this character, then any value of n above 50 agrees with the results as closely as they are themselves known.

Now the equation[22] connecting x and T (absolute), is

$$R \log_e x = \Delta C_p \log_e \frac{(T_{F_0} - \Delta t_F)}{T_{F_0}} - \frac{L_{F_0} - \Delta C_p (\Delta t_F)}{(T_{F_0} - \Delta t_F)} + \frac{L_{F_0}}{T_{F_0}}$$

which if $\triangle$ Cp, the difference in thermal capacity at constant pressure of crystalline and dissolved carbon should happen to be zero, becomes

$$R \log_e x = \frac{-L_{F_0}}{T_{F_0}} \frac{\Delta t_F}{T_F}$$

or

$$\log_{10} x = \frac{-0.4343 \; L_{F_0} \; \Delta t_F}{R T_{F_0} \; T_F} \qquad (4)$$

where R is the gas constant 1.98 calories and L_{F_0} and T_{F_0} are the latent heat of fusion and freezing point of the excess constituent of the solid solution.

T_F is the figure previously called T in this paper and

$$\triangle t_F = T_{F_0} - T$$

Substituting these values we may write

$$\log_{10} x = -0.224 \left(\frac{L_{F_0} T_{F_0}}{T_{F_0} T} - \frac{L_{F_0} T}{T_{F_0} T} \right)$$

$$= -0.224 \left(\frac{L_{F_0}}{T} - \frac{L_{F_0}}{T_{F_0}} \right)$$

$$= -0.224 \; L_{F_0} \frac{1}{T} + 0.224 \frac{L_{F_0}}{T_{F_0}} \qquad (5)$$

[22] Washburn, "Principles of Physical Chemistry," p. 168.

and comparing (5) and (1)

$$A = -0.224\ L_{F_0} \tag{6}$$

$$B = \frac{0.224\ L_{F_0}}{T_{F_0}}$$

$$= -\frac{A}{T_{F_0}} \tag{7}$$

From (6) and (7) we may calculate L_{F_0} and T_{F_0} assuming the values of n of Table VII and the corresponding calculated constants A and B.

Table VIII

n	L_{F_0}	T_{F_0} (abs.)
0.125	4870	−800
0.250	4839	−600
0.500	4785	−1200
1.0	4683	−2060
2.0	4486	−3900
4.0	4134	−1540
25.0	2285	3650
50.0	1491	3000
100.0	884	2700
1000.0	107	2400

The quantity used by Washburn, L_{F_0}, in his derivation for the lowering of the freezing point means the latent heat of fusion. Its analog in a study of saturated solid solution is the heat of solution of the excess phase (per mol.).[23]

The value T_{F_0} represents the temperature at which $x = 1$, i.e., where carbon is infinitely soluble, assuming that the same laws continue to apply. Very obviously this temperature is very high for the condition is not even approached at the eutectic melting point. We can have no knowledge of its true value. Values of n near 25 would therefore seem more plausible than higher values.

Wark's results[24] for the solubility of carbon in the metastable system are:

[23]Tammann and Oelsen, "Die Abhängikeit der Konzentration gesättiger Mischkristalle von der Temperatur," *Zeitschrift für anorganische und allgemeine Chemie*, Vol. 186, 1930, p. 257.

[24]Wark, "Bestimmung der Loslichkeitslinie des Eisencarbids (Fe_3C) in gamma-Eisen," *Metallurgie*, Part 22, 1911, p. 704.

Table IX

T in Degrees Cent.	Solubility in Per Cent Carbon
1070	1.65
1035	1.59
1015	1.55
990	1.50
970	1.45
935	1.32
885	1.21
710*	0.85*

*These figures are not from Wark but represent an average of the probable eutectoid values.

Empirically these figures represent the equation $Y = 0.00257 - 0.00326\ C + 0.00213\ C^2 - 0.000499\ C^3$ (8) where Y is the reciprocal of the absolute temperature and C the solubility of carbon in per cent.

T. M. Chapman has computed from these data the best equations of the form

$$\log x = \frac{A}{T} + B \qquad (1)$$

for various values of n_1, when n_1 has a meaning corresponding to n in the previous derivation. The values of A, B and the probable error were as follows:

Table X

n_1	A	B	Probable Error Per Cent Carbon
1	−1196	1.858	0.021
2	−1123	0.067	0.021
4	−1002	0.211	0.014
8	− 825	0.270	0.010
25	− 474	0.212	0.006
50	− 291	0.142	0.004
100	− 165	0.084	0.002
1000	− 19	0.010	0.000+

From these values we may derive values of L_{fo} and T_{fo} as before:

Table XI

n_1	L_{Fo}	T_{Fo}
1	5420	negative
2	5060	16700
4	4480	4700
8	3680	3050
25	2110	2280
50	1300	2050
100	730	1960
1000	84	1900

From Table X any value of n above 8 is as accurate as the fundamental data can be expected to be. We do not know much about plausible values of T_{F_0} but would suppose that this constant would be lower than that for carbon. Further, it would seem that the value for n in both solutions, austenite and boydenite, should be the same unless carbon and cementite contain different numbers of atoms of carbon per molecule. The values of T_{F_0} in the above table are lower than those for equal values of n in Table VIII for all values of n above 25. Since 25 was also formerly a plausible value of n, that value or one near it, appears to be indicated.

It was desired to determine whether equation (8) can by some suitable selection of n, be made identical with an equation of the form of (1). We may transfer Y to the right side of the equation and divide by 0.000499, the coefficient of C^3 and then obtain the roots of this equation by well known methods[25]. The only real value of C which satisfies equation (8) is approximately

$$C = 1.424 + (4.50 - 2000\ Y)^{1-3} \qquad (9)$$

and the problem becomes whether by suitable selection of n_1 the ratio of the number of iron atoms per molecule to the number of carbon atoms per molecule of cementite we can obtain from the above values of the molar concentration of cementite, x, consistent with (1).

The derivation in Appendix B shows this to be impossible.

It is recognized that the data of other observers with respect to the A_{cm} line might yield a different value of n_2. Thus Tammann and Oelsen (loc. cit.) consider that the agreement with the logarithmic relation of Honda and Endo's magnetic data is satisfactory assuming apparently that Fe_3C and Fe are the correct molecular formulae. The Honda and Endo determinations are shown in Table XII:

Table XII

Temp. Degrees Cent.	Mol. Per Cent Fe_3C
1070	7.83
995	6.93
945	6.15
900	5.84
840	5.25
710	4.06

[25]Claudel, "Handbook of Mathematics," p. 247.

and Tammann and Oelsen's equation, not here quoted because of a slight difference in form of expression, agrees with the data with a probable error of 0.02 per cent carbon, the basis of their calculation being equivalent to the postulate that $n_1 = 1$. By raising n_1 to 10 the probable error can be reduced to about 0.007 per cent carbon and the value 4000 ± absolute will be obtained for T_{F_0}.

Of late the A_{cm} line is frequently drawn as a straight line joining the points having the coordinates

$$C = 0.85\%\,;\ T = 710°C.$$

and

$$C = 1.70\%\,;\ T = 1130°C.$$

and thus having very nearly the equation

$$C = 0.002\ T - 0.57 \qquad (10)$$

The equation derived by Bates and Lawson,[26] although of slightly different form, agrees rather closely with this.

The rectilinear equation above written can not, of course, be theoretically identical with a logarithmic relation but involves a probable error of but little over 0.001 per cent carbon if $n_1 = 1$ or if $n_2 = 10$. The rectilinear representation of A_{cm} thus permits of as little as a single atom of carbon per molecule so far as agreement with the form of equation is concerned. The value $n_1 = 1$ gives a negative value for T_{F_0} but $n_1 = 10$ a value of about 3200 degrees Cent.

The substitution of other data for those of Wark thus permit, but do not require, lower values of n on the score of precision. The value $n_1 = 1$, however, leads to an impossible conclusion although $n_1 = 10$ is an admissible value.

The preceding discussion has furnished us a ratio between the molecular weight of carbon (of Fe_3C) and iron rather than absolute values. We can never deduce, mathematically, from solubility data true molecular weights unless that constant is known for either the solvent or solute.

There appears no reason for assuming a different molecular weight of iron in the two solutions, hence the values of n deduced

[26] Bates and Lawson, "Metastable Equilibrium in Hypereutectoid Iron-Carbon Alloys," TRANSACTIONS, American Society for Steel Treating, Vol. 18, pp. 659-669.

above may be expected to be inversely as the number of carbon atoms per molecule of solute. The probability of equal values of n then represents a similar probability of equality of carbon atoms per molecule of solute. Since we must thus abandon the lattice cell as a unit of measurement, the assumption of single atoms of carbon per molecule is the simplest.

Excluding very high temperatures monatomic elements should approach the value 6.2 calories for the atomic heat.[27] The atomic heat of iron in the range from zero to 918 degrees Fahr., is 8.79 according to Durrer.[28] The atomic heat at 918 degrees Fahr. would be considerably greater since the atomic heat is less at lower temperatures. This exception to Du Long and Pettit's law with regard to the atomic heat of iron would seem to demonstrate either that iron was polyatomic or else the effect of temperature upon the electrons of the iron atom was very considerable.

An objection to the entire preceding line of argument is recognized. If the changed thermodynamic environment produced by increasing concentration in the solid solutions is sufficient to destroy the basis of equation (1), our entire reasoning is invalidated.

Our calculations show that over the limited range accessible to experimentation an equation of the form of (1) does apply but it is conceivable that this is mere coincidence and that the true equation for very dilute solutions has the same form but a different set of constants. Recognizing this possibility, the present discussion is put forward as a suggestion for further study and not as an established hypothesis.

An independent method of ascertaining the appropriate constants would form a valuable basis for a conclusion as to the degree to which the A_{cm} and A_{gr} lines do conform to the theoretical form.

Solute in Austenite

It is shown in Tables VIII and IX that the latent heat of solution per molecule of carbon and Fe_3C is nearly alike for all equal values of n and n_1, the calculated values being usually slightly higher in the latter case. Postulate the same solute monatomic carbon in both cases and similar dispersion in the lattice. The heat of solution of an atom of carbon from cementite in austenite should differ from

[27] Washburn, "Principles of Physical Chemistry," page 257.

[28] Landolt-Börnstein, "Physikalisch-chemische Tabellen," Julius Springer, 1923, page 1243.

that from carbon in boydenite by the heat of formation of cementite, for before carbon can be dispersed atomically, Fe_3C must be destroyed. Since this difference does not exist, the postulated identity in kind and position of the solute can not exist, again confirming the lack of identity, in kind, of austenite and boydenite.

Attention is invited to the similarity of position of carbon in relation to six surrounding iron atoms in cementite according to Hendricks[29] and in austenite.

Conclusions

It is believed that the preceding discussion justifies the following conclusions:

(1) Graphitization is a phenomenon occurring in as nearly pure binary alloys as are obtainable.

(2) If graphitization can occur at a given temperature, it can also occur at any higher temperature at which solid alloy may exist.

(3) Graphitization can occur at 650 degrees Cent. (1200 degrees Fahr.) but there may be a lower limiting temperature below which cementite is stable. Data are not available for calculating this limit if it exists.

(4) Austenite and boydenite are distinct in kind and not identical when of the same carbon concentration.

(5) The thermal data show no evidence of the decomposition of Fe_3C on passing into solution in austenite.

(6) Reasons exist for not attempting to show without further evidence that solid iron is monatomic.

Appendix I

Let n_1 be the ratio $\dfrac{\text{Atoms of iron per molecule Fe}}{\text{Atoms of carbon per molecule } Fe_3C}$

Let C be the solubility of carbon in %.

x be the solubility of carbon as molfraction of Fe_3C

$$x = \frac{\dfrac{15\ C}{180}}{\dfrac{15\ C}{180} + \dfrac{100 - 15\ C}{56 n_1}} = \frac{56\ Cn_1}{56\ Cn_1 - 180\ C + 1200}$$

[29] Hendricks, "The Crystal Structure of Cementite." Reprint from *Zeitschrift für Kristallographie*, Vol. 74, No. 5/6, 1930.

$$\text{If } \log x = AY + B \quad \frac{d^2 \log x}{dY^2} = 0$$

$$\frac{d \log x}{dY} = \frac{1}{x}\frac{dx}{dY} = \frac{56\,Cn_1 - 180\,C + 1200}{56\,Cn_1}\,\frac{d}{dY}\frac{56Cn_1}{56\,Cn_1 - 180\,C + 1200}$$

$$= \frac{400\,C}{(56\,Cn_1 - 180\,C + 1200)\;C\,(b + cY)^{\frac{2}{3}}} \quad \text{If } C = a + (b + cY)^{\frac{1}{3}}$$

Where Y is the reciprocal of the absolute temperature

$$\frac{d^2 \log x}{dY^2} = \frac{-400\,C}{dY}\,\frac{d\,(56\,Cn_1 - 180\,C + 1200)\;C\,(b + CY)^{\frac{2}{3}}}{[(56\,Cn_1 - 180\,C + 1200)\;C\,(b + CY)^{\frac{2}{3}}]^2} = 0$$

The denominator is finite for finite values of C, Y and n_1 hence

$$\frac{d\,(56\,Cn_1 - 180\,C + 1200)\;C\,(b + CY)^{\frac{2}{3}}}{dY} = 0$$

$$\frac{C}{3}\left\{C(112Cn_1 - 360C + 2400)(b + CY)^{-\frac{1}{3}} + (112Cn_1 - 360C + 1200)\right\} = 0$$

$$(112n_1 - 360)[a^2(b + CY)^{-\frac{1}{3}} + 3a + 2(b + CY)^{\frac{1}{3}}] + 1200[2a(b + CY)^{-\frac{1}{3}} + 3] = 0$$

$$n_1 = \frac{120}{112}\left(3 - \frac{20a(b + CY)^{-\frac{1}{3}} + 30}{a^2(b + CY)^{-\frac{1}{3}} + 3a + 2(b + CY)^{\frac{1}{3}}}\right)$$

Hence no single constant value of n_1 satisfies the conditions.

$$\text{Let } n = \frac{\text{Atoms in a Fe molecule}}{\text{Atoms in a C molcule}}$$

C = Carbon (%)

x = Carbon (molfraction)

$$= \frac{56\,Cn}{(56n - 12)\;C + 1200}$$

Y = Reciprocal of absolute temperature

If $(C + a)(Y + b) = K$ and $\text{Log } x = AY + B$ then

$$\frac{d^2 \text{Log } x}{dY^2} = 0$$

$$\frac{d\,\mathrm{Log}\,x}{dY} = \frac{(56n-12)C+1200}{56\,Cn}\,d\cdot\frac{56\,n\,(K-ab-aY)}{(56n-12)(K-ab-aY)+1200(Y+b)}\,\frac{1}{dY}$$

$$= \frac{(56n-12)\,C+1200}{56\,Cn}\,\frac{-\,67200\,nK}{[(56n-12)(K-ab-aY)+1200(Y+b)]^2}$$

$$= \frac{-\,1200\,K}{(K-ab-aY)\,(\alpha-\beta Y)}$$

If $\alpha = (56\,n-12)\,(K-ab)+1200\,b$ and

$\beta = a\,(56\,n-12)-1200$

$$\frac{d^2\,\mathrm{Log}\,x}{dY^2} = \frac{1}{dY}\,d\cdot\frac{-\,1200\,K}{(K-ab-aY)\,\alpha-\beta Y)}$$

$$= +\,1200\,K\,\frac{ab\beta-a\alpha+2\,a\beta\,Y-K\beta}{(K-ab-aY)^2\;(\alpha-\beta Y)^2} = O$$

If $ab\beta - a\alpha + 2a\beta Y - K\beta = O$ then $\alpha = O$ and $\beta = O$

If $\alpha = O\;n = \dfrac{12\,(K-ab)-1200b}{56\,(K-ab)} = \dfrac{1200+12a}{56a} = n$ If $\beta = O$

Hence $K = O$ If α and β are both zero.

If $(\alpha-\beta\,Y)^2 = \infty$,

$\alpha - \beta Y = (56n-12)\,(K-ab-aY)+1200\,(b+Y) = \pm\,\infty$

$n = \pm\,\infty$

Acknowledgments

The writer's thanks are due to the U. S. Bureau of Standards and especially to Mr. Louis Jordan for furnishing the nearly pure metal samples; to the Cleveland Wire Division of the General Electric Company and especially to W. P. Sykes for the glass work involved in their heat treatment and to Messrs. G. M. Guiler, H. H. Johnson, C. H. Junge and T. M. Chapman for the execution of experiments and calculations involved in the paper.

DISCUSSION

Written Discussion: By Yap, Chu-Phay, physical metallurgist and chemist, 27 Grove St., New York City.

This important and significant paper by Mr. Schwartz is to be welcomed

and the American Society for Steel Treating may be congratulated for the opportunity of having him present this paper before its convention. Aside from the established reputation of the author of this paper, its serious and scholarly treatment alone merits full consideration from all of us.

Much of the material included in the paper covers also my main studies in the past two years or so. Unfortunately some of my results do not appear to be in agreement with Mr. Schwartz' conclusions and I merely present them for his and your consideration.

I. The terms "stable" and "stability" need to be properly defined. I think the free energy concept offers us the most reliable index of stability and we may say a compound is stable if its free energy of formation is negative and a fairly large quantity, because a reaction always goes spontaneously in the direction of maximum diminution of free energy. Thus as Lewis and Randall[1] aptly call it, the free energy change is the driving force which indicates the direction in which a reaction may take place.

It has been erroneously held for a long time that the heat of formation is a criterion of the stability of the compound, because it was assumed that the higher the heat of formation, the larger the chemical affinity of the elements forming the compound. Although the falsity of this conception of Bertholet (who, however, very happily chose the most appropriate term of "maximum work") was immediately shown by van't Hoff and others, it, nevertheless, persists to this day because in many cases it is quite true that, for example, an endothermic compound is unstable. Because we know that the heat of formation of Fe_3C is always endothermic up to very high temperatures, we erroneously assume it to be consequently unstable. It may or may not be so, and only free energy calculations will decide this point.

II. With that in view I have made a thorough study of the free energy of formation of Fe_3C from room temperature to as high as 1400 degrees Cent., but unfortunately a technical society to which I submitted my paper rejected it. Incidentally I should like to say that I have evolved a simple graphical method of obtaining the equilibrium constants necessary for the calculation of the $\triangle F$ values, which appear to give far more reliable results than direct experiments. In order not to complicate my discussion, I shall merely enumerate a few of my conclusions:

(a) I found that Fe_3C in equilibrium with saturated austenite (above the A_1 temperature, of course) is stable above about 850 degrees Cent. (The concept of Fe_3C in contact with pure alpha iron above the A_1 point is purely fictional and has no physical meaning.) Cementite is accordingly unstable at 650 degrees Cent.

(b) I found also that Fe_3C in equilibrium with saturated austenite becomes increasingly more and more stable as the temperature increases. Proof that $\triangle F$ of the formation of Fe_3C is a large negative quantity is simply the fact that when carbon is added to molten iron and then quenched rapidly afterwards, we obtain Fe_3C and not carbon. To use a slightly incorrect but more easily understood term, the chemical affinity of iron and carbon must be great enough

[1]G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," 1923, McGraw-Hill Book Co., New York.

to drive them to combine. The degree of dissociation of pure Fe_3C melt can be easily calculated from the value of $\triangle F = -RT \ln K$, where K is simply the mass-action constant. However, in the presence of excess iron, as in hypoeutectic iron-carbon alloys, Fe_3C should be dissociated only very slightly in the melt.[2]

(c) In the reaction, $3(a)Fe + C = Fe_3C$; $\triangle F_{298} = 9500$ cal./mol (tentative value). The positive quantity indicates that Fe_3C is unstable at room temperature.

(d) From the vapor pressure data (of CO/CO_2) I found that somewhere between 1000 and 1100 degrees Cent., a change in the austenite may occur, as suggested by my detailed analysis of the magnetic data obtained by Honda and Endo.[3]

III. The breakdown of Fe_3C by annealing is not itself proof of the unstability of the compound, at least from a strictly thermodynamic point of view. If we place a piece of iron in steam at, say 1000 degrees Cent., so that the reaction

$$Fe + H_2O = FeO + H_2; \quad \triangle F_1 \qquad (1)$$

takes place, we do not customarily claim that H_2O as such is unstable. Reaction (1) takes place to the right until equilibrium is established, because the free energy of reaction ($\triangle F_1$) is negative and a fairly large quantity. I am not claiming that Fe_3C is stable at all temperatures; I wish merely to point out the thermodynamic implications of the word *stable*, as it is generally used.

IV. Although unimportant, I should like to call attention to the fact that further graphitization of the pure iron-carbon samples Mr. Schwartz used in his study does not appear to constitute sufficient proof that no gas is *adsorbed* in the graphite in the sample before the anneal. In fact, the presence of graphite in the sample is sufficiently strong proof of the probable presence of gases in the sample. The sticking of the sample to the glass (inner) tube may be due to the expansion of the sample and the absence of any outward deformation of the glass tube may be due to the higher pressure outside it (that is, in the silica tube), according to their own admission.

While I cannot entirely subscribe to the theory of Professors Honda and Murakami regarding the catalytic influence of the carbon oxides, because catalysis, by definition, implies the mere acceleration of a chemical reaction which would otherwise take place only very slowly, I quite agree with them that graphitization at high temperatures is probably due to the presence of *absorbed* or *adsorbed* carbon oxides in the alloy.

V. In a paper accepted for publication by this society, I have obtained an A_{cm} line expressed in terms of per cent carbon by weight by the equation

$$\%C = 2.17 \times 10^{-3}t - 0.767 \qquad (2)$$

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[2]Consult, for example, the complete transcript of discussion to my paper on "A Thermodynamic Study of the Phasial Equilibria in the System: Iron-Carbon" Technical Publication No. 381, American Institute of Mining and Metallurgical Engineers, which will probably appear in the yearly TRANSACTIONS.

[3]Honda and Endo, "Influences of Dissolved Carbide on the Equilibria of the System: Iron-Carbon," Technical Publication No. 382, American Institute of Mining and Metallurgical Engineers, 1931.

At A_1 (720 degrees Cent.) C = 0.795 and at 1130 degrees Cent., C = 1.685 per cent carbon. The apparently equilibrium values I have derived involve the use of a method which implies that the A_3 and A_{cm} points were obtained at infinitely slow rates of heating and cooling. I only give equation (2) here as a matter of interest.

VI. If I may suggest, a much simpler thermodynamic equation governing solubility directly derived from the unintegrated form of the van't Hoff reaction isochore is

$$\frac{d \log x}{d(1/T)} = \frac{\Delta H}{2.3R} \qquad (3)$$

By plotting x (molar concentration of the *solute*) against 1/T, the slope of the curve thus obtained should give the heat of solution. Assuming an ideal solution, the integral and differential heats of solution should be identical. I have also shown in a paper submitted elsewhere that carrying the conception a little further, we should find in an ideal solid solution that the heat of solution in the solid should be also identical to the heat of solution of the solid solute in the melt (that is, the heat of fusion). I found this actually to be the case[4] and calculated the heat of fusion of Fe_3C to be about 5720 cal./mol, without introducing any correction due to ΔC_p.

The agreement between the heat of fusion and the heat of solution of Fe_3C in austenite appears to be very strong evidence that the solute in austenite (at least, up to about 1020-1050 degrees Cent.) is Fe_3C, as the solute in the melt is Fe_3C.

VII. In the same paper, I have also attempted with negative results to investigate the possibility of iron being soluble in Fe_3C according to Mr. Schwartz' previous suggestion. When there is solid solubility at both ends of the diagram, equation (2) must be modified by introducing the distribution constants thus:

$$\frac{d \log(x/x')}{d(1/T)} = \frac{\Delta H}{2.3R} \qquad (4)$$

since the solute in contact with the solution (liquid or solid) is no longer pure, but has a molar concentration of x'. When there is no solid solubility at the other end of the diagram, then x' = 1 and drops out and equation (4) reverts to equation (3).

VIII. The reputation of Watase and Roth (especially the latter) for very careful work is well-known and their values of the heat of formation of Fe_3C varying from 2.5 to 3.9 Cal./mol, however different compared to the values obtained by others, nevertheless, warrant careful consideration. Recalculating the values of Brodie, Jennings and Hayes on the basis of Roth's latest and apparently more accurate values of iron oxides, I obtained the following figures: 12,367, 13,670 and 12,220 cal./mol. The first and the last check within

[4]This is not the only case, as I have shown in my paper on "A Thermodynamic Study of the Equilibria of the Systems: Antimony-Bismuth and Antimony-Lead," Technical Publication No. 397, American Institute of Mining and Metallurgical Engineers, 1931, that the heat of solution antimony in lead is identical to its heat of fusion.

allowable experimental error, and since the value of the second one is about 1300 calories off, we may reject it and accept the mean value of 12.3 Cal./mol as the heat of formation of Fe_3C at 25 degrees Cent. (actually at 30 degrees Cent.).

From the fundamental free energy equation,[5] $\Delta F = \Delta H - T\Delta S$, we calculate ΔF when we know ΔH and ΔS, the entropy of formation in the present case. Giving only rough figures (sufficient for our present purpose of illustration) ΔS is about 10 entropy units and if ΔH is taken as 12.3 Cal., then

$$\Delta F_{298} = 12{,}300 - (298 \times 10)$$
$$= 9320 \text{ cal./mol.}$$

which is in rough agreement with the value given in II (c). On the other hand if we used Roth's value ΔH value of 3.9 Cal./mol, we obtain $\Delta F_{298} = 920$, which would make Fe_3C only very slightly unstable. Using Watase's later value of 2.5 Cal./mol, $\Delta F_{298} = -480$ cal., which would make Fe_3C stable at room temperature. Although I was at first inclined to give the lower values more consideration, I must now set myself on record that in spite of Roth's and Watase's careful work, their values appeared to be in great error, unless Fe_3C is very much less unstable than it is at room temperature. The fair agreement between the work of Ruff and his co-workers and the work of Hayes and his co-workers and the results of my own free energy study, all indicate that the value of 12.3 Cal./mol probably represents the best value.

IX. I regret very much to be unable to agree with Mr. Schwartz' hypothesis regarding the existence of boydenite; I would like to believe in its existence, because it would simplify many of my calculations. There should be more than one comparatively easy method of proving the existence of boydenite. If we hold a steel at a temperature above A_1 sufficiently long enough, then the austenite should eventually transform to boydenite, which when quenched and tempered should precipitate carbon (graphite). Consistent with Honda's theory of hardening of quenched steel, they assume the solute to be carbon and consequently they held, until only very recently, that the precipitated carbon then combines to form Fe_3C at some range of temperature (about 300 to 400 degrees Cent.). Since ΔF is positive from room temperature up to at least A_1, it is difficult, therefore, to conceive the recombination of iron and carbon to Fe_3C. It seems to me that, aside from other sources of evidence, and there is considerable, the fact that we always obtain Fe_3C in steels tempered at low temperatures, is very strong evidence that the solute in austenite is Fe_3C and not carbon, as I have already shown from an analysis of the magnetic data obtained by Honda and Endo (*loc. cit.*).

As I have already mentioned above, evidence is gradually accumulating that around 1020 to 1050 degrees Cent., there may occur a transformation in austenite, in which above that temperature, the solute, at least in terms of chemical energetics, should be considered as carbon and not Fe_3C. The change may be conceived to be brought about as follows: it is only reasonable, on the basis of

[5]It is perhaps needless to point out that Mr. Schwartz' calculation of the maximum work realizable from the heat of formation is incorrect. According to him, $\Delta S = 0$, so that $\Delta F = \Delta H$. This is the Bertholet principle of maximum work.

our X-ray evidence, to assume that the carbon on the Fe_3C occupies the center of the face-centered cube. X-ray crystal analysis, at least at the present stage of development, is unable to describe the force field of the carbon atom with respect to the other atoms, so that all we can say is that at any instant the force field of three iron atoms and one carbon atom is such that we must consider the existence of a Fe_3C molecule. The disruption of this molecular force field due to the large thermal agitation does not involve any rearrangeemnt of the austenite lattice, as the relative positions of the six iron atoms occupying the faces of the cube to the carbon atom in the center still preserve the stoichiometrical relation of the compound $6(\frac{1}{2}Fe) + C = Fe_3C$. Such a picture of a transformation of austenite[6] also precludes the existence of boydenite, which implies a substitutional type of lattice.

In conclusion I should like to explain that if the tone of this discussion appears to be rather dogmatic, it is because I have given only certain conclusions drawn largely from my unpublished papers. I felt great hesitancy at first in contributing this discussion, because it might appear that I do not appreciate the enthusiasm and interest of Mr. Schwartz, but the larger claims of science would not be served by anything less than an honest appraisal of his paper, nothwithstanding my personal feelings and high esteem for him. The industry with which he is associated is fortunate to have a leader so advanced in viewpoint and so receptive to new ideas and new methods. Finally, any criticism I have made of Mr. Schwartz' paper should not detract one whit from its merits nor obscure its significance.

Author's Closure

The discussion presented by Yap, Chu-Phay should contribute materially to the interest of the writer's paper. In so far as the discussor has amplified the paper with additional information frequently without having space for a complete exposition of the root sources of his ideas further discussion by the author is perhaps unnecessary. There remain a few points which apparently constitute actual difference of opinion on matters connected with the interpretation of the diagram concerning which a reply is called for even though in making this reply the author must extend the discussion beyond the confines of the original paper.

To the writer it appears that the terms "stability" and "metastability" are so well understood that no confusion is likely to arise in the minds of any metallurgist sufficiently well informed to be at all interested in the subject matter of the original paper. There should be no confusion between the stability of a compound formed from its constituents by a first order or monomolecular action and a second order reaction such as the formation of iron oxide from iron and steam which the discussor cites as an instance of the decomposition of the compound water in a temperature range where that compound is stable.

We probably all understand already that any reaction proceeds, it at all, in that direction corresponding to the liberation of energy. If the reaction is between two elementary components of a compound this means clearly that the compound is stable or unstable dependent upon whether energy is liberated

[6]Plans are now under way to study this subject by means of X-ray analysis.

when it is formed or when it is decomposed. It means also that a reaction occurring spontaneously indicates by its direction the algebraic sign of the free energy change Δ F. It does not follow, however, that the absence of a reaction proves the stability of the existing system; the classic text book illustration being that hydrogen and oxygen do not combine at room temperature even though water is a stable compound at that temperature. It is not clear, therefore, why the discussor in Section III should not consider the breaking down of cementite into its constituents as evidence of instability.

The criticism that the true measure of stability is found in the free energy of formation rather than in the heat of formation of the compound is entirely justified. It happens, however, that the writer knew of no very reliable determinations of the former constant and also wished to bring into the picture the information derived from the Japanese specific heat data. That the free energy data are in a somewhat confused state, may be judged from Note 11 of the discussor's paper, "Influence of Dissolved Carbide on the System Iron-Carbon," Technical Publication No. 382, American Institute of Mining and Metallurgical Engineers. Here Mr. Yap, does not give us sufficient information to show why he gets values different from Messrs. Maxwell and Hayes. The reasoning, whatever it may be, is somewhat vitiated by the fact that his data are "consistent with Watase's low value of 4800 calories at room temperature" (for the heat of formation of cementite), while in the present discussion of the writer's paper in Section VIII Mr. Yap, himself sets out reasons for rejecting the data of Watase and of Roth for the heat of formation in favor of the results of Messrs. Brodie, Jennings and Hayes. The writer will recur a little later to some further implications of the free energy of reaction.

Lacking adequate knowledge as to Δ F the writer hoped to gain some idea of the stability of the system from the heats of formation correcting as indicated for, the energy change corresponding to the irreversible expansion of the iron in graphitizing which change does not occur during the calorimetric combustion of cementite as such. As evidence that such a course is not altogether without merit we may quote, from Mr. Yap (loc cit page 6) "we know that Fe_3C is endothermic compound . . . and we have, therefore, *good reasons* to believe that the change in the free energy (Δ F) of the formation of Fe_3C . . . is also plus in sign." So far as the writer knows, computations of Δ F for the formation of cementite have always been based upon studies of the gas equilibria in the systems CO-CO_2 or CH_4-H in contact with free carbon and with cementite. The leading authority in this field is presumably Rudolph Schenck, who, after twenty-five years of research and after correcting a previous erroneous opinion to the contrary, finally located these equilibrium curves with such relative positions that the curve representing the equilibrium with cementite departs from that representing the equilibrium with carbon in the direction of higher CO concentrations at lower temperatures. The relative positions of these two curves prove that cementite is always unstable within the temperature range for which the reaction has been studied. We need not calculate values of Δ F to prove this but need consider only the following.

At a given temperature the gas in equilibrium with Fe_3C is richer in carbon monoxide than that in equilibrium with carbon and the reaction, $2\ CO = C + CO_2$ proceeds where the same gas is in contact with carbon.

Such portions of this gas as come in contact with cementite then react $CO_2 + Fe_3C = 2\ CO + 3\ Fe$ (assuming that no reaction with iron takes place which reaction if it did occur, would represent a different system from that which we are studying). Fe_3C would thus be continuously converted into iron and free carbon and if the reaction will proceed in this direction by the particular mechanism under discussion, it must proceed in the same direction by any other method and in turn it would be impossible to obtain by calculation from the given curves any value of $\triangle F$ which was not of that algebraic sign corresponding to the known direction of the reaction. The work of Schenck thus confirms the observed fact that cementite is unstable in the range from A_1 up to as close to the eutectic melting point as the experiments have been made to extend. The direction of this reaction has been observed frequently; among others by Messrs. Bates and Lawson on vacuum-melted alloys of a fair degree of purity and commercially in the presence of silicon on such an enormous scale that the facts can scarcely be disputed.

Consideration of the fact that the presence of silicon would affect the stability of cementite only if dissolved therein or combined therewith and that in either of the above cases the vapor pressure of carbon from cementite would be lowered by the presence of silicon, the stability of cementite could not be decreased by the element silicon. This is not to say that the speed of the reaction is not greatly altered.

Commenting on the graphitizing of pure iron samples the discussor says in Section IV that he does not feel that the possibility of adsorbed gas in the graphite has been excluded; presumably in a rigidly technical sense this is true. Consider, however, that according to the discussor's viewpoint the liquid melt contains cementite in solution, not graphite; with this thought the writer is in agreement. The metal froze in a fairly respectable vacuum and after freezing is known to contain graphite. Beyond the exceedingly small mass of gas contained in the melting apparatus at low pressure the writer does not see where the graphite got any gas to adsorb nor, being completely enclosed in steel, does he see where this graphite came in contact with any gas which it might have adsorbed during the interval in which it was shipped from Washington to Cleveland. It is the writer's impression that the work at the Bureau of Standards has rather definitely shown that the vacuum fusion method completely degasifiies liquid iron.

It may be repeated that the shape of the glass tubes after graphitization showed that they were collapsed onto the sample, not that the sample had expanded into contact. The absence of any gas bubbles would seem to prove that the higher pressure on the outside was able to force the glass against the metal without leaving any measurable accumulation at the pressure which the gas in the silica tube had. The discussor's suggestion that, after all, detectable amounts of gas might be present, might therefore be ignored as not consistent with experimental observation.

With regard to the solubility of iron in cementite referred to in the discussor's fourth section, it may be said that some recent work by other methods has shown compositions such as encountered by Messrs. Bates and Lawson do indeed exist. It will be shown in a paper to be published later how these substances are related to cementite.

The lack of graphitization in steel above the A_3 point, although not yet clearly explained, may not prove the stability of austenite or cementite in this field. It has already been pointed out that reactions will not always start even though they desire to proceed in some particular direction.

The persistence of cementite in cast irons quenched in the liquid state is another instance in point. The presence of this cementite does not prove that cementite is stable and does not want to decompose but only that for lack of time or other considerations it does not do so. The co-existence of certain phases in an unchanging system proves nothing as to their stability unless we know that this system is in equilibrium. Usually we know this only if we have been able to observe changes in the system with time. In so far as there is a difference of opinion between Mr. Yap and the author, that difference seems to arise entirely out of the question of whether or not cementite is ever stable at temperatures, say above 800 degrees Cent. The discussor maintains that cementite is stable on the ground of certain free energy calculations which he has made. In the original paper the writer has given possibly inconclusive reasons for considering it thermodynamically unstable. The writer further believes that this latter conclusion has the merit of being confirmed not only by direct experimentation but also by the available data regarding gas equilibria. Neither of the two latter points were included in the original paper merely because the author was not attempting to deal with all possible aspects of this problem which in the aggregate constitute only a part of the subject matter of the original article.

Although profoundly convinced of the importance of thermodynamics in the study of metallurgy, the writer cannot refrain from sounding a note of warning. Thermodynamic considerations are frequently somewhat complicated and obscure to the point where even very able students unconsciously are led astray. Observers of the first rank have occasionally reported data subsequently found not to apply to the particular reactions or systems which were believed to have been realized and errors of reasoning are not altogether impossible. One of the best tests for the validity of any particular discussion is, therefore, whether the known facts confirm the conclusions. When a conclusion is reached not in harmony with the accepted facts then one of three things has happened. The facts are not as they were supposed to be, the reasoning has been erroneous, or the reasoning was based on inaccurate assumptions. In other words we cannot start from the truth and by correct reasoning get anything but a truthful conclusion.

The writer does not understand all the successive steps by which the discussor arrives at his conclusions; this is in part due to the brevity with which these conclusions were dealt with in the discussion and in part, perhaps, also is a reflection upon the author's knowledge of thermodynamics. Under these circumstances he cannot say whether in his opinion the error resides in the original data or in the use that was made of it but feeling fairly sure of the ultimate facts, not only on the grounds of the present paper but for other reasons discussed above, he has very grave doubts of a conclusion which the discussor is defending and sees no reason to alter his opinion that cementite is unstable at all temperatures above the lowest at which its unstability has been observed.

NONDEFORMING ALPHA-DELTA CARBURIZING STEEL

By A. B. Kinzel

Abstract

Observation indicates that the largest factor relating to distortion involved in quenching of carburized steel is the volume change produced by phase changes in the core. Accordingly, carburizing steel has been produced, in which the core has been rendered free from phase changes by additions of suitable amounts of alpha-forming elements such as silicon, vanadium, and chromium. These steels were found to carburize readily, the case being rendered austenitic by the increased carbon content. Thus, at temperature before quenching, the article consists of an austenitic case and a ferritic core. The tests show that with this combination distortion on quenching is a minimum. Core properties have been improved by the combination of chromium and silicon, with the probable formation of silicides, so that a steel has been produced which is suitable for industrial application where nondistortion is the prime factor.

DISTORTION in hardening carburized members has long been a problem to the steel treater and producer. Most attempts to minimize this distortion have consisted in lowering the hardening temperature by lowering the critical point of the steel. This is accomplished by introducing into the steel, gamma-forming elements such as nickel and manganese, and retained austenite also helps to reduce the distortion. Considerable progress has been made in this direction.

Distortion on quenching carburized specimens is due to a number of causes, the principal one being the effect of strains caused by differential volume changes as various points in the article pass through the transformations at different times and temperatures during the quenching. Another factor in distortion is the strain due to normal temperature gradients throughout the mass, but this is probably much less important than the first mentioned cause. For ex-

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, A. B. Kinzel, is a member of the society and is associated with the Union Carbide and Carbon Research Laboratories, Long Island City, N. Y. Manuscript received June 18, 1931.

ample, quenching a specimen of 0.02 per cent carbon iron from approximately 800 degrees Cent. (1470 degrees Fahr.) results in very little distortion, even though the section be nonuniform. During this quenching, the material undergoes no transformations, as it is entirely ferritic at the quenching temperature. Thus the ideal nondistorting steel would be one without allotropic transformations. This, of course, presents a paradoxical condition, as these transformations are necessary for the type of hardening usual in steels, namely, martensite formation. Accordingly, the next best condition would be one in which only that portion of the specimen which is to be hardened undergoes transformations. When this portion of the material is very thin, all of the hardened part undergoes transformation at approximately the same time, a condition not far from the ideal. This condition would be realized in a carburized article with a case which is austenitic and a core which is ferritic at the temperature for quenching. One possible solution would be the use of carburized iron with less than 0.04 per cent carbon in the core. This piece as a whole could then be quenched from approximately 800 degrees Cent. (1470 degrees Fahr.), the core at this temperature being ferritic, the case being austenitic. This solution is impractical due to the extremely low core strength which results. If the carbon exceeds approximately 0.04 per cent, the material when heated to the eutectoid temperature, nominally 700 degrees Cent. (1290 degrees Fahr.), becomes austenitic, at least in part. As the temperature increases, more and more austenite is formed. This is the case with the usual carburizing steels now in use.

It is, however, possible to raise the temperature at which transformation will begin in a steel containing small but appreciable (0.010 per cent) amounts of carbon by means of moderate amounts of alloying additions. If the alloy addition is sufficient, this temperature is increased and the gamma-delta transformation temperature is decreased until the gamma phase is completely eliminated. This is, of course, the well-known austenite loop common to the alloys of iron and alpha-forming elements. The best known examples of this loop are illustrated in the diagrams of the iron-chromium, iron-silicon, iron-vanadium, iron-tungsten, and iron-molybdenum systems. In Fig. 1, a typical "iron-alpha forming alloy" diagram is shown. This diagram is based on very low carbon percentages. As the carbon content is increased, the two-phase region is widened, and the end of the austenite region occurs at higher and higher alloy con-

tents, so that at a high carbon content, such as 0.90 per cent, the amount of alloy necessary to suppress the gamma transformation becomes very great indeed. A typical diagram for such an alloy is shown in Fig. 2. Free carbides are omitted from the diagrams. If we now consider a carburized alloy article of composition X in Figs. 1 and 2, it will be readily seen, as shown in Fig. 1, that at 800 degrees Cent. (1470 degrees Fahr.) the core material is completely ferritic and may be cooled to room temperature without transfor-

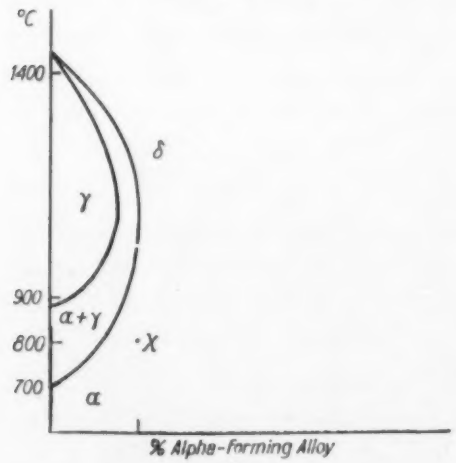

Fig. 1

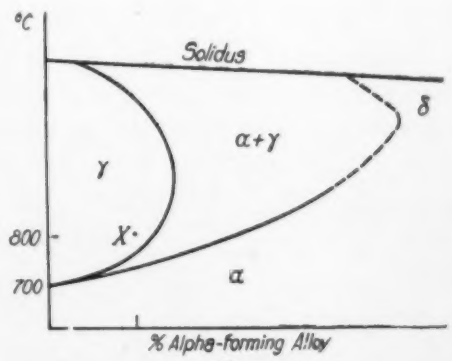

Fig. 2

Fig. 1—Diagram for Iron with 0.10 Per Cent Carbon with Alpha-forming Alloy.
Fig. 2—Diagram for Iron with 0.90 Per Cent Carbon with Alpha-forming Alloy.

mations. On the other hand, the case material represented in Fig. 2 is austenitic, and on quenching should form the type of ferrite typical of quenched steel,—martensite, troostite, or sorbite, depending on the quenching rate. This case and core combination then fulfills the requirements set forth for a carburizing steel which will undergo minimum distortion.

The problem of synthesizing such an alloy presented several phases. As stated above, the production of alloys which are wholly ferritic depends entirely on alloying with the proper amount of alpha-forming elements so that this part of the problem is readily solved. The next question which arises is the process of carburizing. Only very small amounts of carbon are soluble in ferrite, so that it should not be possible to carburize a ferritic steel. To investigate this, a steel was made with high silicon content, and a carburizing test carried out. Study of the microstructure showed that the ferrite takes up a certain amount of carbon at the usual carburizing temperature (900 degrees Cent.) (1650 degrees Fahr.). This is sufficient to

Table 1
Alloy Content and Physical Properties of Alpha-Delta Steels

Heat No.	Alloy Content—Per Cent Si	Cr	V	W	Zr	Core Properties Yield Point Lbs. sq. in.	Ult. Strength Lbs. sq. in.	Elong. in 2 in. Per Cent	Red. of Area Per Cent	Case Hardness Oil Quenched —1 in. rd. Rockwell "C"
1	2.31	1.04	...	...	...	53,000	77,000	28	62	62
2	1.55	1.21	...	...	0.40	32,000	63,000	35	71	62
3	1.31	0.84	0.26	...	...	58,000	86,000	32	65	65
5	2.08	1.21	0.13	...	...	51,000	83,000	29	64	64
6	1.47	1.27	0.19	...	...	40,000	81,000	28	46	60
7	2.04	...	0.67	...	...	35,000	58,000	35	74	62
8	1.05	...	0.47	...	...	50,000	66,000	38	78	62
9	1.45	1.27	0.14	...	0.23	35,000	67,000	36	68	61
10	1.52	0.62	...	1.45	...	43,000	91,000	23	35	62
11	1.84	...	...	...	...	.....	.....	..	..	65

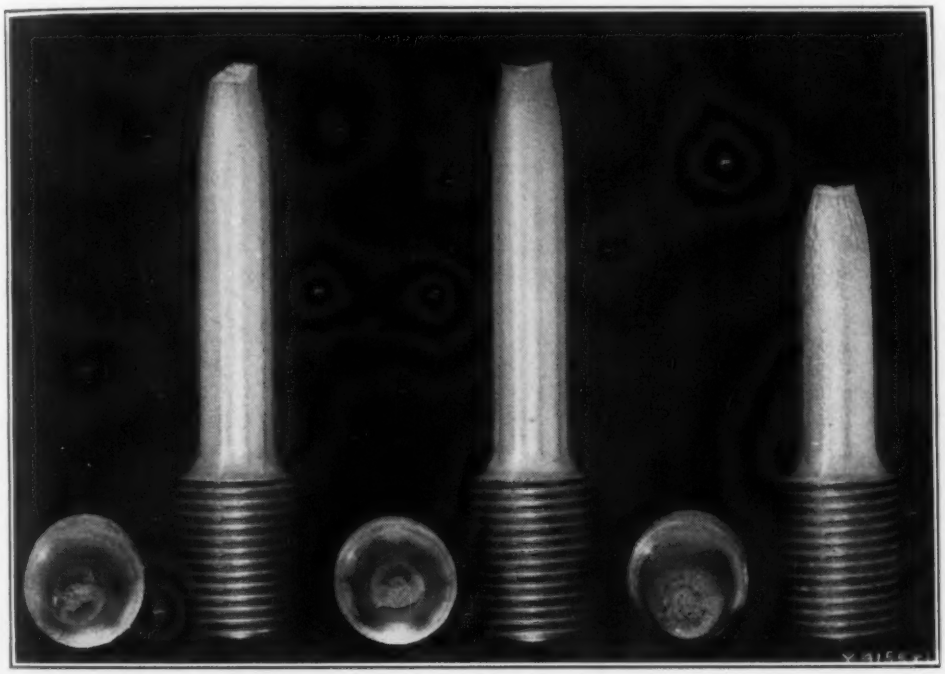

Fig. 3—Tensile Specimens as Heated at 900 Degrees Cent. (1650 Degrees Fahr.), Furnace-cooled and Quenched from 800 Degrees Cent. (1470 Degrees Fahr.). Heat Nos. 1, 5 and 2 Respectively.

cause the ferrite to change to austenite. Accordingly, much more carbon is taken up and passed on to the adjacent ferrite which changes to austenite, and the process continues, the whole taking place at such a rapid rate that the limiting factor in the carburizing is not the allotropic state of the steel, cases of the same depth being produced in about the same time as in the usual austenitic steels.

The next question involved was the matter of obtaining satis-

factory core properties under the above limitations. Accordingly, a number of iron alloys with maximum 0.10 per cent carbon with certain of the usual alpha-forming elements were made in a 6-pound induction furnace. Silicon was favored because of its low cost, and chromium because of its hardening action and the probable formation of chromium silicide which should improve the core properties.

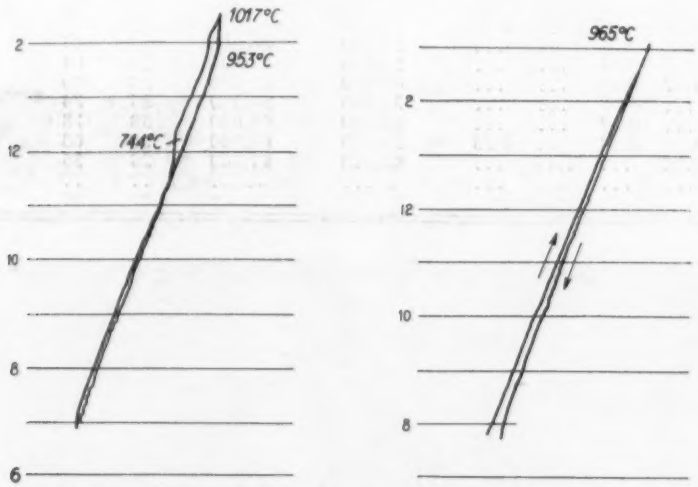

Fig. 4—Dilatometer Curves on Specimens from Heats Nos. 4 and 7 Respectively.

Vanadium and tungsten were used for their grain refining influence. Zirconium is an alpha-forming element, known to increase shock resistance. Table I shows the alloy content of the heats and the core properties after carburizing and quenching treatments. Tensile specimens from heats 1, 5, and 2 are shown in Fig. 3. Although the yield points and ultimate strengths are not as great as is usually obtained with commercial carburizing steel, they are sufficient for many purposes where lack of distortion is the prime requisite.

To further check the correctness of the theories above advanced, a study of the core materials was made with a dilatometer which had been so arranged that temperature dilation curves were obtained directly. The curves for two of the heats in question (4 and 7) are shown in Fig. 4. That for heat 4 containing 0.93 per cent silicon, 0.48 per cent chromium and 0.49 per cent vanadium, shows the way in which a critical point is indicated, and that for heat 7 shows a typical curve on material free from transformations. Carburized temperature gradient bars were quenched in order to determine the proper treating temperature.

Fig. 5—Photomicrograph of Case Produced on Alpha-delta Steel No. 10. Original Magnification × 100, Reduced 40 Per Cent in Making Reproduction.

These bars showed that the maximum hardness occurred at the points which had been at 800 degrees Cent. (1470 degrees Fahr.). Specimens of the heats in question were then carburized as 1-inch rounds, oil-quenched from 800 degrees Cent. (1470 degrees Fahr.), and tested for hardness and microstructure. The Rockwell hardness figures given in Table I show that the requisite hardness is obtained. A typical photomicrograph of the case, a specimen from heat 10, is shown in Fig. 5. This is self-explanatory, and indicates usual character and 0.07-inch depth of case after carburizing at 900 degrees Cent. (1650 degrees Fahr.) for 12 hours.

Tests for distortion were then carried out on carburized specimens oil-quenched from 800 degrees Cent. (1470 degrees Fahr.). Photographs of the two types of distortion test specimens are shown in Fig. 6. The first of these is a slender round bar, and the second a disk with an eccentric hole and slot. The bars were placed on accurate centers and measured for straightness. Distortion of the disks was measured in the microscope with gage marks across the slot. Within the limits of accuracy of the measuring instrument, 0.0005 inch, no distortion could be noted on the slotted disks, and the bars showed a maximum deviation from straightness less than one-tenth of that obtained on a similar bar of plain carbon steel with core containing 0.15 per cent carbon. This checks the theories and expectations in this matter.

Discussion

The fact that an article with a hard, deep case may be produced with minimum distortion on quenching, renders it probable that commercial applications for this material will be found. Due to the nature of the steel, certain specific precautions and practices will be required in connection with particular applications. The lack of transformation in the core means that a more careful attention to finishing temperature on rolling is necessary, although the use of grain refining elements such as vanadium, will undoubtedly cut down troubles from this source. Although the work here described was carried out on small heats, there is sufficient background on this practice so that it may be definitely stated that the results are indicative of those to be obtained in larger heats, and that probably even better properties may be expected from the larger heats. As to specific compositions, much depends on the specific application. It would

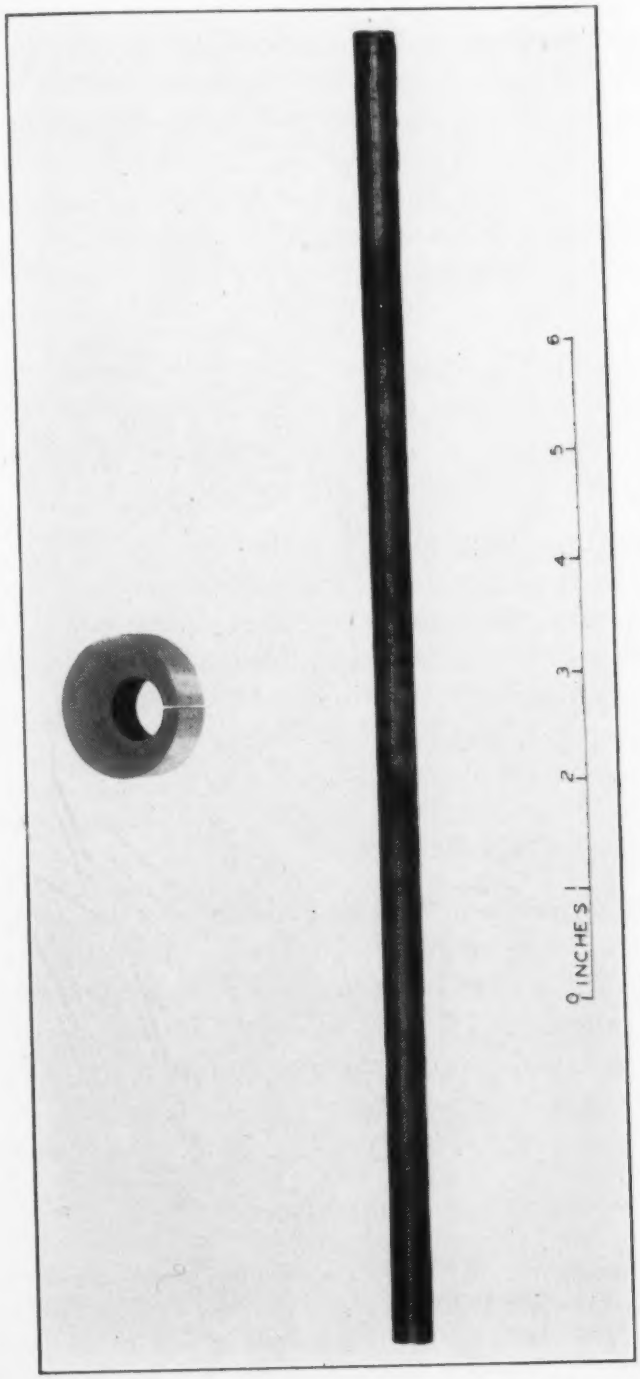

Fig. 6—Photograph of Distortion Test Specimens.

seem, however, both from economic and technical considerations, that the iron-silicon-chromium base is desirable. To this base, vana-

dium should be added, as it is particularly effective in the control of grain size. The writer believes that with further work in connection with specific applications where all the requirements and limitations of the problem are known, it will be possible to further augment the yield point and ultimate strength of the core, and that the basic principle evolved is susceptible of application.

Conclusions

The following conclusions are based on the work herein reported, and are, of course, subject to modification as work on a larger scale progresses. However, the first three items are of such a nature as to be independent of conditions of production.

1. Alpha-delta steel may be carburized.
2. The core properties of alpha-delta steel are unaffected by the carburizing treatment if suitable analysis is chosen.
3. A carburized article with a gamma case and alpha core has the minimum tendency to distort on quenching.
4. Chromium-silicon-vanadium steels are suitable for many non-deforming carburized parts.

Acknowledgment

The author wishes at this time to express his appreciation of the interest and stimulation given by J. H. Critchett, vice president of the Union Carbide and Carbon Research Laboratories, Inc., as well as the generous assistance rendered by his colleagues at the laboratories, and wishes to particularly mention the work done by John J. Egan in carrying out the program.

DISCUSSION

Written Discussion: By O. W. McMullan, metallurgical department, Timken-Detroit Axle Co., Detroit.

The author has worked out an interesting theory for carburizing steels. A steel without the gamma transformation in the core should decrease warpage and volume changes even more than low temperature quenches on the ordinary steels as changes in the latter of course take place as soon as the Ac_1 point is reached which must be exceeded to harden the case.

There does, however, seem to be the possibility of a very sharp dividing line between the martensitic expansion of the case and complete lack of such

expansion in the core. Might not this set up stresses which would produce grinding checks or exfoliation in service? The core also remains in its original nonhomogeneous condition as shown in Fig. 5 which may cause brittleness. A uniform sorbitic structure in a core is much more shock resistant than a mixed structure of ferrite and pearlite whether partially hardened or not. Control of grain size of the special steels to keep them fine-grained would mostly eliminate such brittleness. Fine-grained steels of the ordinary type distort much less than coarse-grained steels, but this would probably have little or no influence on the special steels.

Written Discussion: By I. N. Zavarine, assistant professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

The author should be congratulated on his clear presentation of the principles underlying the production of a case hardened article with hardenable case and nonhardenable core, also the possibility of producing a series of alloy steels satisfying such requirements. The method itself is a well established art in the production of cyanided malleable iron castings.

A consideration of the physical properties of the core of alpha-delta steels presented by the author in Table I leads to speculation regarding the probable field of application of such steels. A steel with an alpha-delta core will be inherently a low strength material, a fact which apparently will exclude such steels from applications to highly stressed parts. The principal advantage of these steels over hardenable alloy steels should be expected in their nondeforming properties on quenching. These properties should have been demonstrated more convincingly by the author.

Written Discussion: By George M. Enos, assistant professor, department of chemical engineering, University of Cincinnati, Cincinnati.

This extremely interesting and valuable paper may point the way to overcoming some of the difficulties encountered in the quenching of carburized steel. The author is to be congratulated for his excellent work.

One or two questions arise in connection with the text and perhaps Mr. Kinzel can help the reader to a better understanding. On page 440 it is stated "a steel was made with high silicon content, and a carburizing test carried out." What was the analysis of this steel?

It is very interesting to note the statement that the "limiting factor in carburizing is not the allotropic state of the steel." No comment is made as to whether the carburizing test was tried at higher or lower temperatures than 1650 degrees Fahr. Further information as to time required, depth, and character of the case formed might be of interest.

On page 442, in the discussion of Fig. 4, reference is made to numbers "945" and "907." These numbers do not appear on the graph.

Author's Closure

The discussions received in connection with this paper are all of a constructive and stimulating type, and the author wishes first to thank the discussers for their thought and comments. In Fig. 5 a typical continuous photomicrograph is shown. The transition zone from core to case is small, but not

unduly so, and as yet no difficulties due to exfoliation, as anticipated by Mr. McMullan, have been experienced. In general it is true that sorbitic structure is the most shock resisting. It is entirely conceivable that a ferritic structure would be equally shock resisting, provided the ferrite were strengthened by precipitation of material other than carbides. Experiments herein reported show that this is the case with the steels in question. We agree with Mr. McMullan as to the effect of fine grain, and are glad that he stressed this point.

Mr. Zavarine's analogy of the cyanided malleable iron castings is excellent, although it may be argued that there is a prime distinction in the two methods due to the presence of free carbon which can go into solution in the iron if the temperature is higher than usual. In the fully ferritic steels this is not possible. That a ferritic or alpha-delta core is inherently a low strength material is not necessarily true, although it is true in the absence of certain special alloying elements. Table I shows strength ranging from 80,000 to 90,000 pounds per square inch, and such values certainly cannot be considered to represent low strength material. Moreover we believe it possible to increase this strength, provided all the other factors involved in a given application are known. Professor Zavarine is entirely correct in stating that the principal advantage of these steels is to be expected in their nondeforming properties on quenching. The tests performed to demonstrate this nondistorting property, using specimens shown in Fig. 6 in the paper, were quite convincing to us. However, only direct application to specific problems will show the full importance and magnitude of this effect.

The silicon steel referred to by Dr. Enos was chosen at random and was known to contain more than 2.5 per cent silicon. The steel was not specifically analyzed as it was simply a pilot test to study the carburizing phenomena. The only essential feature was that silicon be high enough to keep the steel ferritic at all temperatures. Carburizing tests on the various steels in question were only tried at 1650 degrees Fahr., as no difference was noted in the carburizing performance in these steels and the usual austenitic steels. Higher temperatures would cause undue grain growth and lower temperatures would reduce the rate of carburizing in at least the usual well known manner. Thus we did not see any great point in studying this phase of the problem.

In conclusion we would like to stress the fact that, while these steels have certain limitations due to their very nature, they also have certain very marked advantages, and that there are no doubt many applications where the limitations will not be serious and the advantages will be decidedly worth while.

AGING IN LOW-CARBON STEELS

By A. Allan Bates

Abstract

This paper describes in some detail relationships between quenching temperature and aging ability of extra soft steels. The degree of age-hardening of which low carbon steel is capable may be compared favorably with that of duralumin and other aluminum alloys. The author points out that this aging is due largely to precipitation (submicroscopic) of carbides within the ferrite grains and the resulting hardness in the steel is inversely proportional to the individual particle size of the precipitate.

25 or 30 days are usually required for precipitation, but this time may be greatly reduced if the steel is heated to a comparatively low temperature, for example, 30 minutes at 100 degrees Cent. has a distinct effect. If the steel is slowly cooled from temperatures near the A_1 point or if it is tempered for a suitable period at temperatures of 100 degrees Cent., age-hardening may be entirely avoided.

AMONG the most interesting of the physical properties of certain aluminum alloys such as duralumin is their capacity for age-hardening at room temperature after suitable heat treatment. During the past decade this phenomenon has been thoroughly investigated by metallurgists in both the United States and Europe and its causes are now thought to be fairly well fixed and understood. In view of the importance of this age-hardening to the aluminum industry and of the amount of study which has been expended upon it, and in view of the simplicity of the theory concerning its underlying cause, it is perhaps strange that the possibility of a similar aging in iron and steel has received so little attention. It has, indeed, been frequently remarked that the hardness and ductility of certain steels may occasionally change in notable if not discomfiting fashion

This paper constitutes a resumé of certain portions of a research project carried out by the author at the Ecole Superieure de la Métallurgie et de l'Industrie des Mines at Nancy, France, in partial fulfilment of the requirements for the Doctorate of Science at the University of Nancy.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, A. Allan Bates, is a member of the society and is instructor in metallurgy, Case School of Applied Science, Department of Metallurgy, Cleveland. Manuscript received June 12, 1931.

during a certain period of time after the steel has been put into use, although no incidental "heat treatment" or mechanical work can have intervened to account for the mysterious change.

One of the first careful investigations of the aging of steel was that made by Masing and Koch in 1928. A review of their results was published in *Stahl und Eisen,* August 2, 1928. These investigators found that a low carbon steel quenched rapidly from 660 degrees Cent. (1220 degrees Fahr.) would increase from about 120 to 190 Brinell during the course of a 16-day aging at 20 degrees Cent. They suggested that this was the effect of a precipitation hardening of the same type as that which occurs in duralumin. Later work tended to show that any one of a number of elements present in the steel might cause the age hardening. Most notable among these elements are carbon, nitrogen and oxygen. In 1930 *(Le Genie Civil,* September 13, 1930) Professor Seigle of Nancy published an interesting memoir relating to certain strange results which he had obtained during the course of an investigation of extra soft basic Bessemer steels. In brief, Seigle found that the aging power of this steel was very marked after a quench at 700 or at 900 degrees Cent. (1290-1650 degrees Fahr.) but that it was comparatively small after quench at 800 degrees Cent. (1470 degrees Fahr.). (See note below.)

The present paper takes up in detail the relationship between quenching temperature and aging ability of extra soft steel. It proposes a theory to account for this peculiar relationship and gives a brief account of a number of experiments out of which this theory grew. All the work of this research was carried out on an extra soft basic Bessemer steel of the following composition:

	Per Cent
C	= 0.026
S	= 0.032
Mn	= 0.34
Si	= 0.03
P	= 0.07

Normalized at 975 degrees Cent. (1790 degrees Fahr.) this steel has the following mechanical properties:

Ult. Tensile Strength	= 60,200 lb. per sq. in.
Elastic Limit	= 42,200 lb. per sq. in.
Elongation % in 3.5 cm.	= 38.4%
Hardness (Pomey)	= 103

In order that all the results might be strictly comparable, all the experiments were made on test pieces of the same dimensions. These were in the form of a heavy wire (5 millimeters in diameter). The properties investigated were ultimate tensile strength, elastic limit, ductility and hardness.

NOTE: The writing of the present paper had been completed before the author's attention was called to the work published by Köster in "Archives für das Eisenhüttenwesen," 2, 503 (1929). Köster's work is discussed by Mehl and Briggs in their written comment at the end of this article.

Relation Between Quenching Temperature and Aging Ability

For the first series of experiments to be described here, eight tensile test specimens were quenched in each 50-degree temperature interval between 600 and 1000 degrees Cent. (1110 and 1830 degrees Fahr.). Four specimens of each group were tested immediately after

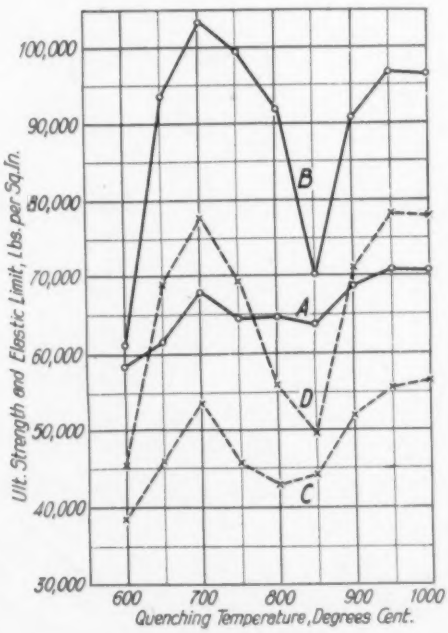

Fig. 1—Shows the Results on the Tensile Strength and the Elastic Limit as Shown in Table I. A—Tensile Strength After Quenching. B—Tensile Strength After Quenching and Aging. C—Elastic Limit After Quenching. D—Elastic Limit After Quenching and Aging.

the quench and four others were set aside to age during a period of thirty days. The aging temperature varied between 9 and 15 degrees Cent. with an average very close to 12 degrees Cent. (54 degrees Fahr.). Preliminary experimentation had shown that aging is complete after twenty-five to thirty days at these temperatures. At the end of this period the remaining bars were tested.

In Table I are shown the average values for tensile strength and elastic limit determined by this experiment. Agreement among the individual bars of each group was in every case very satisfactory. In Fig. 1 are plotted the results on the tensile strength and the elastic limit shown in Table I. The very strong maxima of aging power

which occur at 700 and at 950 and 1000 degrees Cent. and the sharp minimum at 850 degrees Cent. are striking when thus represented graphically. In Fig. 2 are plotted the variations in ductility which in this work was measured by the per cent elongation in 3.5 centimeters.

Table I

Quenching Temperature Degrees Cent.	Tensile Strength lb. per sq. in.		Elastic Limit lb. per sq. in.		% Elongation in 3.5 cm.	
	After Quench	After Quench and Aging	After Quench	After Quench and Aging	After Quench	After Quench and Aging
600	58,200	61,300	38,600	45,300	37.2	29.6
650	61,800	93,600	45,700	68,900	32.9	23.7
700	68,100	103,500	53,700	77,900	31.8	22.6
750	64,900	99,600	45,700	69,400	31.5	20.6
800	65,000	92,000	43,100	56,100	28.1	20.5
850	64,100	70,500	44,800	49,800	23.0	20.5
900	66,800	90,100	52,100	72,400	24.5	19.2
950	71,000	97,000	55,600	78,400	24.3	17.8
1000	71,000	96,100	56,600	78,000	23.6	18.1

The same experiment was repeated in order to determine the variations in hardness brought about by quenching and aging. The hardness was measured by a new apparatus developed by two French engineers, Pomey and Voulet. Briefly, the method consists of pressing a diamond cone into the polished surface of the test piece under the constant pressure of carefully calibrated weights. The diameter of the impression is measured under a microscope and the hardness number determined therefrom by means of a simple algebraic equation. The inventors claim that the method gives hardness figures closely comparable to those determined by the Brinell apparatus. The angle at the point of the cone is 136 degrees and, in the case of the steels investigated in this research, the impressions varied between approximately 0.05 and 0.3 millimeter. For a detailed description of the Pomey-Voulet apparatus the reader is referred to *Revue de*

Table II

Quenching Temperature Degrees Cent.	Hardness (Pomey)	
	After Quench	After Quench and Aging
600	117	123
650	140	182
700	145	193
750	136	191
800	131	171
850	147	165
900	144	171
950	154	178
1000	153	180

Métallurgie, May 1929, page 238. In Table II and Fig. 3 are shown the results of the hardness tests. Each figure in the table represents the average of from four to six determinations made on each of two test specimens. The hardness variations are very similar to those shown by the elastic limit and the tensile strength.

A Theory Accounting for Aging of Soft Steel After Quench

A number of possible causes may be suggested to account for the aging of soft steel after quenching. Many of them may be readily dismissed on theoretical grounds. The author followed up several others to a sufficient extent to show their improbability. Seigle has suggested a change in the matter, amorphous or otherwise, which many writers claim must lie in the grain boundaries. As to the "amorphous cement" it can only be said that it is difficult to dismiss something whose very existence has never been proved or disproved. As a matter of fact, the author has shown later in this article that a precipitation of carbides which tend to become concentrated at the grain boundaries does play an important part in the aging. A second suggestion is that a slow, spontaneous relief of the internal quenching strains is the cause of the age-hardening. Several considerations tend to discredit this theory. First, there seems to be no good reason for supposing that the quenching strains should be less after a quench at 850 degrees Cent. (1560 degrees Fahr.) than after a quench at 650 degrees Cent. (1200 degrees Fahr.) Second, Seigle has shown that the aging increases the brittleness of the steel, which is quite contrary to the results which we might expect were the aging caused by the relief of internal strains.

A third possible cause is that a grain growth occurs during the aging. The author has taken photomicrographs at the same magnification ($\times$ 1000) of the same region of a test piece before and after it had been aged. These photomicrographs showed that no measurable difference in any visible dimension of any grain had occurred during the aging. A number of other causes were similarly investigated and dismissed either on the grounds of theoretical improbability or because experimentation showed them to be unlikely.

Finally, in view of the similar phenomenon in the case of the aluminum alloys, there may be proposed the precipitation hardening theory. A number of considerations immediately present themselves

in support of this theory. First, it is now universally accepted that cementite is to a slight extent soluble in alpha ferrite, and that the degree of solubility is a function of temperature of the same type as is the solubility of copper in aluminum. This feature of the iron-carbon equilibrium diagram is well shown in the diagram published in METAL PROGRESS, September, 1930, page 81. Oxygen-iron and

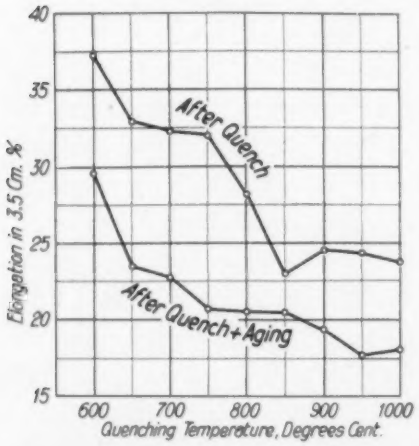

Fig. 2—Shows the Variations in Ductility Which were Measured by the Per Cent Elongation in 3.5 Centimeters.

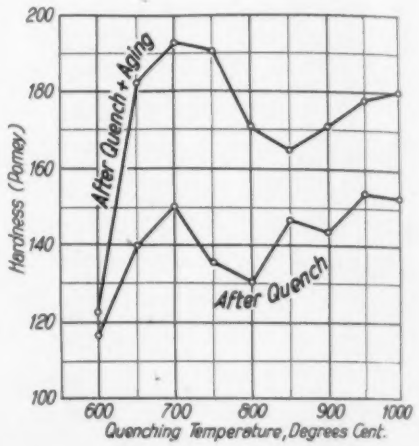

Fig. 3—Showing Results of the Hardness Tests After Various Heat Treatments.

nitrogen-iron alloys have somewhat similar solubility curves. Second, Whiteley[1] has demonstrated that, after suitable treatment, cementite may be precipitated in alpha ferrite in the form of visible particles located within the grains or, in certain cases, at the grain boundaries. Third, consideration of the curves in Fig. 1 in conjunction with the iron-carbon equilibrium diagram brings to light a significant coincidence between the temperatures of quench at which occur the maxima of aging ability (700 and 950 degrees Cent.) and the temperatures of the critical points of low carbon steels.

Convinced by these facts that the aging of steel was most probably an effect of carbide precipitation the author has carried out an extended series of experiments calculated to prove or disprove the theory and, if the theory be found true, to throw some light on the mechanism and control of the carbide precipitation.

The first investigation involved a careful micrographic examination of the test bars which had been treated during the course of the

[1]Whiteley "The Solubility of Cementite in Alpha Iron and Its Precipitation," *Journal*, Iron and Steel Institute, Vol. CXVI 1927 No. II.

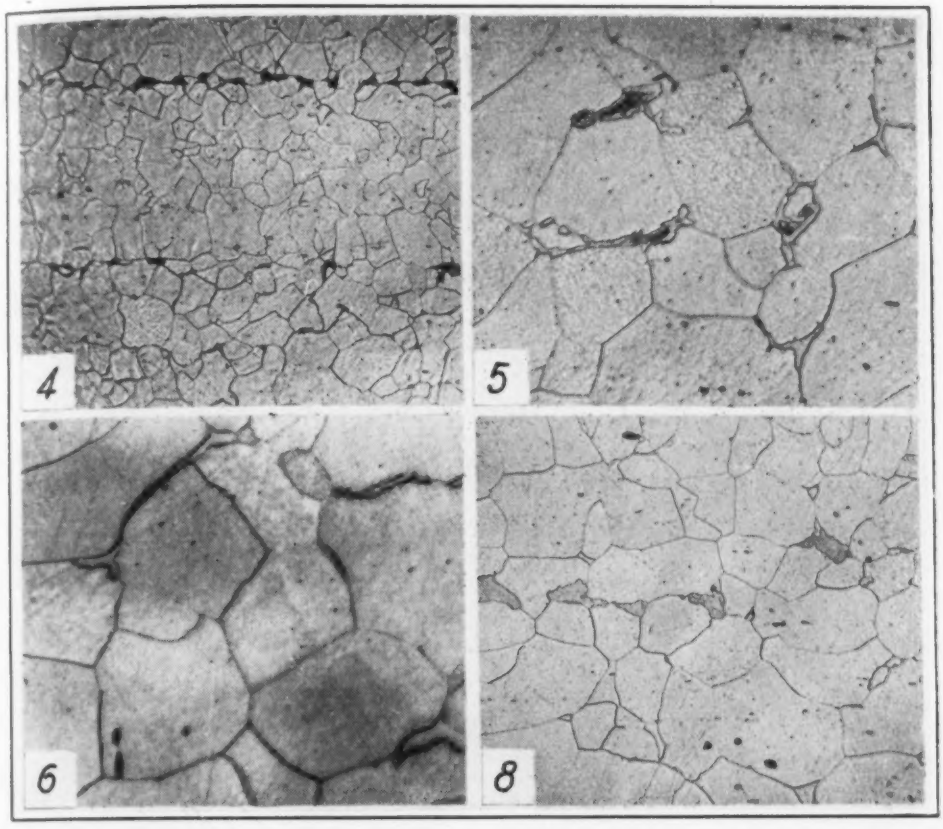

Fig. 4—Low Carbon Steel Normalized at 950 Degrees Cent., (1740 Degrees Fahr.) × 100.
Fig. 5—Same as Fig. 4. × 600.
Fig. 6—Low Carbon Steel Quenched at 700 Degrees Cent., (1290 Degrees Fahr.) × 1200.
Fig. 8—Low Carbon Steel Quenched at 725 Degrees Cent., (1340 Degrees Fahr.) × 225.

experiments described in Table I and Figs. 1 and 2. Absolutely no difference was discoverable in the aspect of these specimens before and after the aging. The examination was carried out at a number of different magnifications varying between 20 and 2000 diameters. Evidently, if there is a precipitation of carbides during the aging, the individual particles of the precipitate are sub-microscopic in magnitude.

From a study of the photomicrographs made during this early investigation a theory has been evolved to account for the peculiar relationship between the temperature of quench and the aging ability of low carbon steel. The reader's attention is first called to Figs. 4 and 5 showing the structure of the steel used in this work after normalization at 950 degrees Cent. (1740 degrees Fahr.). The free

cementite occurs almost entirely in the form of intergranular films. Furthermore, these particles of free Fe_3C are to be found for the greater part segregated in streaks which are aligned parallel to the direction of rolling. The Figs. 4 and 5 were chosen to illustrate the condition of these carbides. To some extent they exaggerate the amount of free carbide actually present in the steel.

After a water-quench at 600 and 650 degrees Cent. (1110 and 1200 degrees Fahr.) no visible change had occurred in the steel.

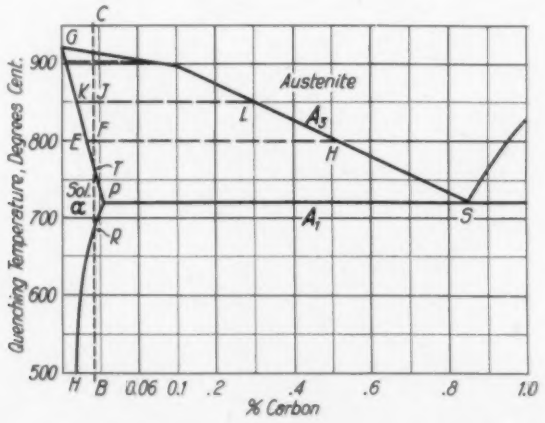

Fig. 7—Reproduces that Portion of the Iron-Carbon Equilibrium Diagram which is of Interest to this Investigation.

After a quench at 700 degrees Cent. (1290 degrees Fahr.) very little free cementite was to be found. The few particles still remaining retained the form of intergranular films. Fig. 6 shows the steel after quenching at 700 degrees Cent. (1290 degrees Fahr.). In Fig. 7 is reproduced that portion of the iron-carbon equilibrium diagram which is of interest to this investigation. The scale of the area between 0 and 0.1 per cent of carbon has been exaggerated for the sake of clearness in the ensuing discussion. The point P is generally thought to lie at about 0.03 per cent carbon. The line PH is usually thought to become vertical below about 500 degrees Cent. (930 degrees Fahr.). Opinion differs widely concerning the carbon concentration of the point H, some metallurgists holding it to be as high as 0.02 per cent carbon, others claiming that it is practically zero. As will be shown later, the present investigation places it between 0.012 and 0.008 per cent carbon. The steel used in this work (0.026 per cent carbon) lies on the vertical line BC.

Now it is evident that, except for a slight progressive diminution

in the amount of free carbide present, no visible change should occur in the structure of the steel on heating, to temperatures below the point R. Between R and T the steel should be a homogeneous crystalline mass of the constituent which the author has called "solution alpha", that is, a solution of Fe_3C in alpha ferrite. At all temperatures below T (about 730 degrees Cent.) the solution alpha so completely predominates the structure of the steel that we must expect its physical properties to determine the physical properties of the metal. If we assume that the strength and hardness of the solution alpha are proportional to its concentration of dissolved carbon, the progressive increase in tensile strength, elastic limit and hardness after quench at temperatures between 600 and 700 degrees Cent. (1110 and 1290 degrees Fahr.) is readily understood. This assumption is quite in accord with the facts found in connection with nearly all alloy systems.

At this point attention must be called to a constituent found after quenching the basic Bessemer steel at temperatures between 710 and 750 degrees Cent. (1310 and 1380 degrees Fahr.). This constituent was made up of small pale gray crystals which were found always aligned in exactly the same position where, before the quench, there had been a streak of free cementite particles. These crystals, which will be called for the moment "Constituent X," always appeared just prior to the final disappearance of free cementite on heating. At no temperature was there found the complete homogeneity called for by the equilibrium diagram between R and T (Fig. 7). After quench at 710 degrees Cent. (and an etch in nital) the Constituent-X was almost white and as homogeneous in internal structure as is the massive cementite found in white irons. Boiling sodium picrate, however, did not darken it. With progressive increase in quenching temperature the Constituent-X became darker in color until, at 760 degrees Cent., it began to show black troostitic edges. At temperatures of quench between 710 and 750 degrees Cent. even a long attack with nital failed to develop in it a sorbitic, troostitic or martensitic structure. It is most unlikely that a pure austenite has been retained in the steel by the treatments which produced the Constituent-X. Having then eliminated cementite, sorbite, troostite, martensite, austenite and, of course, ferrite, there seems to remain only a question mark. More work is being carried out on this subject. Several aspects of Constituent-X are shown in Figs. 8 and 9.

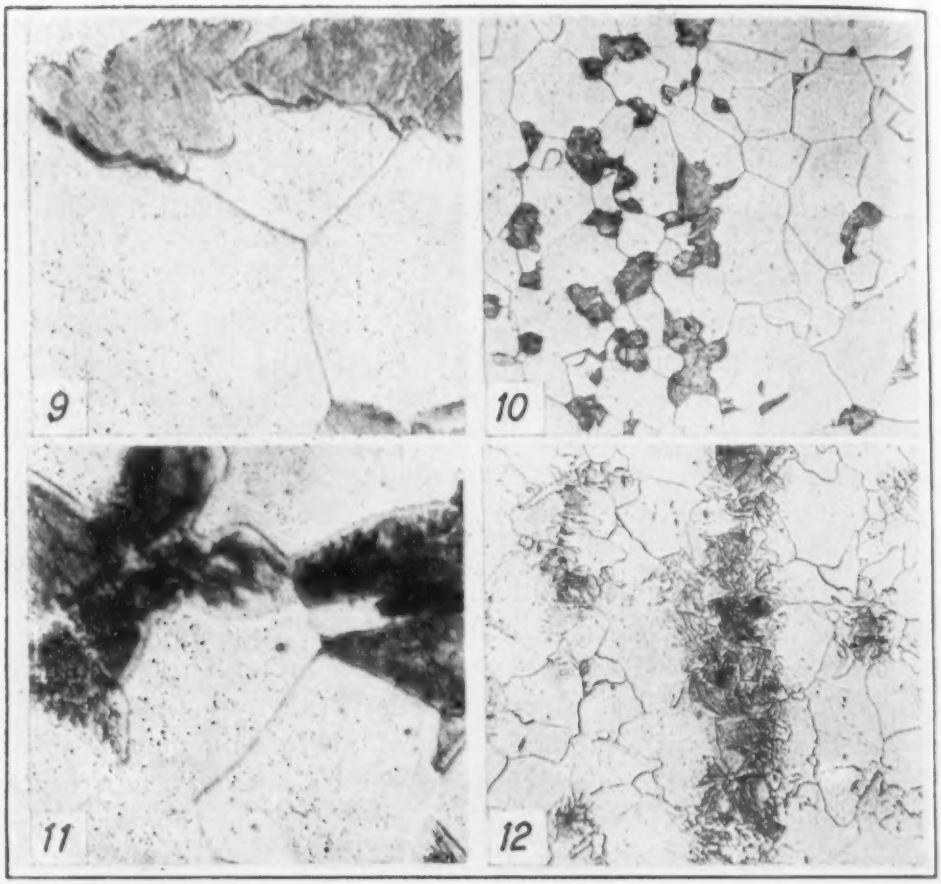

Fig. 9—Low Carbon Steel Quenched at 750 Degrees Cent., (1380 Degrees Fahr.) × 1500.
Fig. 10—Low Carbon Steel Quenched at 800 Degrees Cent., (1470 Degrees Fahr.) × 225.
Fig. 11—Low Carbon Steel Quenched at 800 Degrees Cent., (1470 Degrees Fahr.) × 1500.
Fig. 12—Low Carbon Steel Quenched at 850 Degrees Cent., (1560 Degrees Fahr.) × 225.

Returning now to the discussion of the form of the curves in Fig. 1, as the quenching temperature rises above the point T (Fig. 7) a new area of the equilibrium diagram is reached, an area in which the steel is composed of the two constituents, austenite and solution alpha. The proportions of the two at any given temperature are easily determined in an approximate fashion by means of the equilibrium diagram. Thus at 800 degrees Cent. (1470 degrees Fahr.) the solution alpha constitutes $\frac{FH}{EH}$ or about 95 per cent of the steel. The remaining 5 per cent $\frac{EF}{EH}$ is austenite which after quench be-

comes martensite, (or troostito-martensite). This martensite remains in small grains so isolated as to be unable to affect materially the strength of the steel. On the other hand the carbon concentration of the predominating solution alpha (now of concentration E) has been considerably reduced by the increase in temperature from 700 to 800 degrees Cent. (1290-1470 degrees Fahr.). This explains well why the quench at 800 degrees Cent. has less strengthening effect on the steel than has the quench at 700 degrees Cent. Figs. 10 and 11 show the structure of the steel after quench at 800 degrees Cent. (1470 degrees Fahr.).

If the quenching temperature is raised to 850 degrees Cent. (1560 degrees Fahr.) the proportion of martensite in the steel will be increased to $\frac{KJ}{KL}$, or some 10 to 15 per cent. At this value it begins to become continuous (Fig. 12). These continuous martensitic "fibers" ought to have the effect of increasing the tensile strength of the steel. On the other hand, the solution alpha contains less dissolved carbon than it did at 800 degrees Cent. (1470 degrees Fahr.) and so should be weaker. With these two opposing tendencies the steel, after a quench at 850 degrees Cent. might reasonably be either slightly weaker or slightly stronger than after a quench at 800 degrees Cent., according to the concentration and the distribution of the carbides. Fig. 13 shows the structure of the soft basic Bessemer steel after quench at 850 degrees Cent. (1560 degrees Fahr.).

At 900 degrees Cent. (1650 degrees Fahr.) the steel consists in large part of austenite containing perhaps 0.04 per cent of carbon in solution. On rapid cooling this carbide may precipitate in part as martensitic needles and, furthermore, since this martensitic phase is entirely continuous the steel is appreciably strengthened by this treatment. Nevertheless it is likely that a considerable fraction of the 0.04 per cent of carbon may remain unprecipitated during the quench. At room temperature this carbon is to be found in a state of solution or "suspension" in the alpha ferrite which resulted from the quenching of the austenite. The solution alpha which still exists at 900 degrees Cent. (1650 degrees Fahr.) is very low in carbon but, since it constitutes only a minor portion of the steel, its comparative weakness is more than offset by the low carbon martensite. Figs. 14 and 15 illustrate the structure after quench at 900 degrees Cent. (1650 degrees Fahr.).

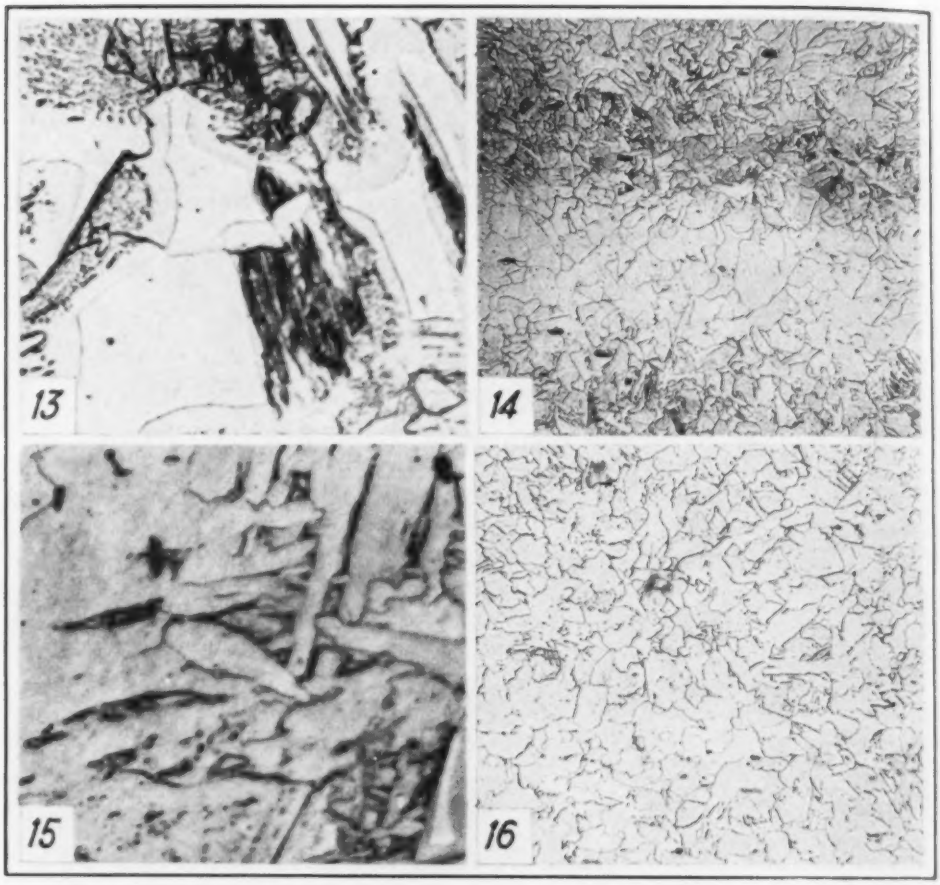

Fig. 13—Low Carbon Steel Quenched at 850 Degrees Cent., (1560 Degrees Fahr.) × 1500.
Fig. 14—Low Carbon Steel Quenched at 900 Degrees Cent., (1650 Degrees Fahr.) × 225.
Fig. 15—Low Carbon Steel Quenched at 900 Degrees Cent., (1650 Degrees Fahr.) × 1500.
Fig. 16—Low Carbon Steel Quenched at 1000 Degrees Cent., (1830 Degrees Fahr.) × 225.

At 950 degrees Cent. (1740 degrees Fahr.) the material is composed entirely of austenite containing 0.026 per cent of dissolved carbon. The quench retains practically all of this very small amount of carbon in solution so that, at room temperature, the steel is in a state closely comparable to that resulting from a quench at 700 degrees Cent. (1290 degrees Fahr.). The quench at 1000 degrees Cent. (1830 degrees Fahr.) is of course essentially the same in its effects as that at 950 degrees Cent. In Figs. 16 and 17 are shown the structure after quench at 950 degrees Cent. (1740 degrees Fahr.).

The entire form of the curve in Fig. 1 which indicates the changes in the physical properties of the steel immediately after

quench is thus explained. With the above facts and assumptions in mind it is not difficult to explain likewise the seemingly peculiar relationship between quenching temperature and aging power.

Below a quenching temperature of about 730 degrees Cent. (1345 degrees Fahr.) (T, Fig. 7) it is necessary to deal only with the solution alpha. It is evident that the degree of supersaturation of this solution at room temperature with respect to Fe_3C is going to become appreciable only after the quenching temperature has risen above the point at which the line PH becomes vertical (500-550 degrees Cent.). From that point on, the supersaturation increases until it reaches a maximum between about 700 and 730 degrees Cent. (1290-1345 degrees Fahr.) (points R and T). The greater the supersaturation the greater the tendency of the carbide to precipitate. The particles of the precipitate lying dispersed throughout the individual crystals either distort or disturb the continuity of the atomic arrangement of the ferrite. The slip interference is thus increased or, otherwise stated, the steel is hardened and strengthened.

The increase of aging power between 600 degrees Cent. (1110 degrees Fahr.) (quenching temperature) and 700 degrees Cent. (1290 degrees Fahr.) together with the marked maximum in the vicinity of 700 degrees Cent. is thus logically explained. Between 700 and 850 degrees Cent. the supersaturation of the solution alpha steadily decreases, becoming almost negligible at 850 degrees Cent. (1560 degrees Fahr.). The martensite which exists after quench at these temperatures can have no appreciable effect on the aging power for two reasons: first, it is very small in amount; second, it represents a phase in which, because of its high concentration, the carbide has already been more or less completely precipitated during the quenching action. The aging power of the steel decreases then between 700 and 850 degrees Cent.

Toward 900 degrees Cent. however the carbide concentration of the austenite becomes quite small (0.04 per cent approximately). It is reasonable to argue that a considerable fraction of this carbide may remain unprecipitated during the quench, resulting, consequently, in a steel which is composed largely of alpha ferrite holding in solution (or "suspension") most of the carbon in the metal. The same argument applies of course even more forcefully to the condition of the metal after a quench at 1000 degrees Cent. (1830 degrees Fahr.). We have in this case (quench at 900 degrees Cent. and

above) essentially the same conditions of supersaturation which obtain after the quench at 700 degrees Cent. and, in consequence, a comparable aging power.

The complete forms of the curves in Figs. 1 and 3 are thus explained. There remain several remarks to be made. First, since the hardness test is made in compression it is not necessary that the martensite be a continuous phase in order to affect this property. The hardness starts rising, then, toward its second maximum at a lower quenching temperature (800 degrees Cent.) than do the tensile strength and elastic limit (850 degrees Cent.). Second, although the general argument in the case of the ductility is the same as in the case of the other properties investigated, it is necessary to bear in mind that the introduction of the nonductile martensite will not cause a rise toward a maximum (as it did, for example, in the hardness) but will, instead, greatly accelerate the drop to a minimum which was already begun by the formation of the supersaturated solution alpha. If the "aging effect" be plotted for each of the four properties investigated, the four curves will be found to be quite parallel.

Accelerated Aging

The aging thus far described took place over a period of thirty days at a temperature of 12 degrees Cent. and in no case did it bring about a structural change in the steel which could be seen under the microscope. Whiteley, in his memoir cited above, found that a visible precipitate of carbides could be produced by quenching a soft steel in the neighborhood of the A_1 line and subsequently drawing it at temperatures between 250 and 600 degrees Cent. Mitinsky[2] has found a similar phenomenon and both writers state that the precipitated carbide has a strong tendency to concentrate in the grain boundaries of the ferrite, particularly if the drawing temperature be above 350 degrees Cent.

It was a matter of considerable interest to determine whether the effects of this visible precipitation are the same as those of the submicroscopic precipitate postulated by the author. It was also of evidently great theoretical interest to determine whether or not the production of the visible precipitate prevented the normal aging from taking place. In order to answer these questions the author quenched

[2]A. Mitinsky, Professor of Metallurgy, School of Mines, Pribrami, Czecho-Slovakia. Private Communication.

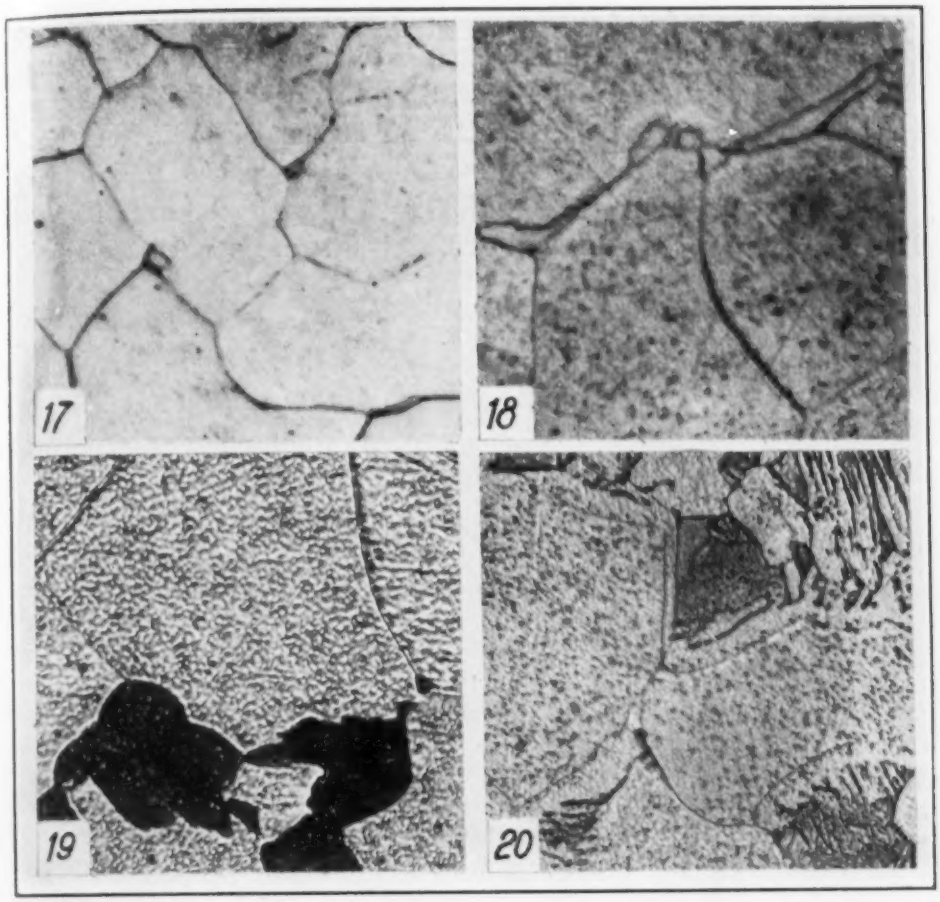

Fig. 17—Low Carbon Steel Quenched at 950 Degrees Cent., (1740 Degrees Fahr.) × 1500.
Fig. 18—Low Carbon Steel Quenched at 650 Degrees Cent., (1200 Degrees Fahr.) Drawn 4 Hours at 225 Degrees Cent., (437 Degrees Fahr.) × 1500.
Fig. 19—Low Carbon Steel Quenched at 750 Degrees Cent., (1380 Degrees Fahr.) Drawn 4 Hours at 225 Degrees Cent. × 1200.
Fig. 20—Low Carbon Steel Quenched at 800 Degrees Cent., (1470 Degrees Fahr.) Drawn 4 Hours at 225 Degrees Cent. × 1200.

six test bars at each of the fifty degree intervals between 600 and 1000 degrees Cent. All the bars were then drawn for four hours at 225 degrees Cent. (440 degrees Fahr.). Three bars of each group of six were tested immediately. The remaining three were tested thirty days later, the temperature having been about 12 degrees Cent. during that interval.

No appreciable difference was found between the bars tested at the different times. Evidently the 4-hour treatment at 225 degrees Cent. entirely prevents the normal aging from taking place. The precipitated carbides were clearly visible in these bars in the form of very fine particles which stood in relief under oblique illumination at

a magnification of 800 diameters or more. Although a very long etch in boiling sodium picrate darkened the more prominent of these particles, a normal etch in 4 per cent nital revealed them much more clearly. In the case of the quenches at 700 and 750 degrees Cent. (1290-1380 degrees Fahr.) the particles were generally so closely packed as to give the ferrite grains a granulated appearance. The photomicrographs, Figs. 18, 19, 20, 21 illustrate several aspects of the precipitate.

The results of the draw at 225 degrees Cent. are shown in Fig. 22, Curve A and Fig. 23, Curve A. Clearly, the visible precipitate has effects altogether different from the "invisible precipitate." This however does not necessarily weaken the hypothesis concerning the invisible precipitate. From the elementary statement of geometry that the volume of a sphere is proportional to the cube of its diameter, it is evident that a given amount of carbide coagulated into comparatively few large, visible particles (which are assumed to be essentially spherical) must cut vastly fewer atomic planes than will the same amount of carbide coagulated into many small invisible spheres. In other words, it is conceivable that the visible precipitate presents no interference to slip on the majority of the atomic planes. The effects of the draw at 225 degrees Cent. were investigated with regard to hardness, tensile strength, elastic limit and ductility. Since the first three of these gave almost exactly the same results only one of them, tensile strength, will be discussed in this paper.

It was thought advisable to determine the effects of several other drawing temperatures and times. Guided by certain preliminary experiments the author employed the following draws:

24 hours at 100 degrees Cent. (210 degrees Fahr.)
48 hours at 80 degrees Cent. (175 degrees Fahr.)
60 hours at 55 degrees Cent. (130 degrees Fahr.)

Longer draws at these temperatures do not alter the results. These treatments were carried out after only those quenching temperatures (700, 850, 950 degrees Cent.) which had given the most interesting results in connection with the normal aging. In every case the accelerated aging completely prevented the subsequent occurrence of the normal aging. After the draw at 100 degrees Cent. the carbide precipitate was clearly visible (See Fig. 24). It is quite noticeable that the different ferrite grains vary in regard to the concentration of precipitate. After the treatments at 80 and at 55 degrees Cent. no

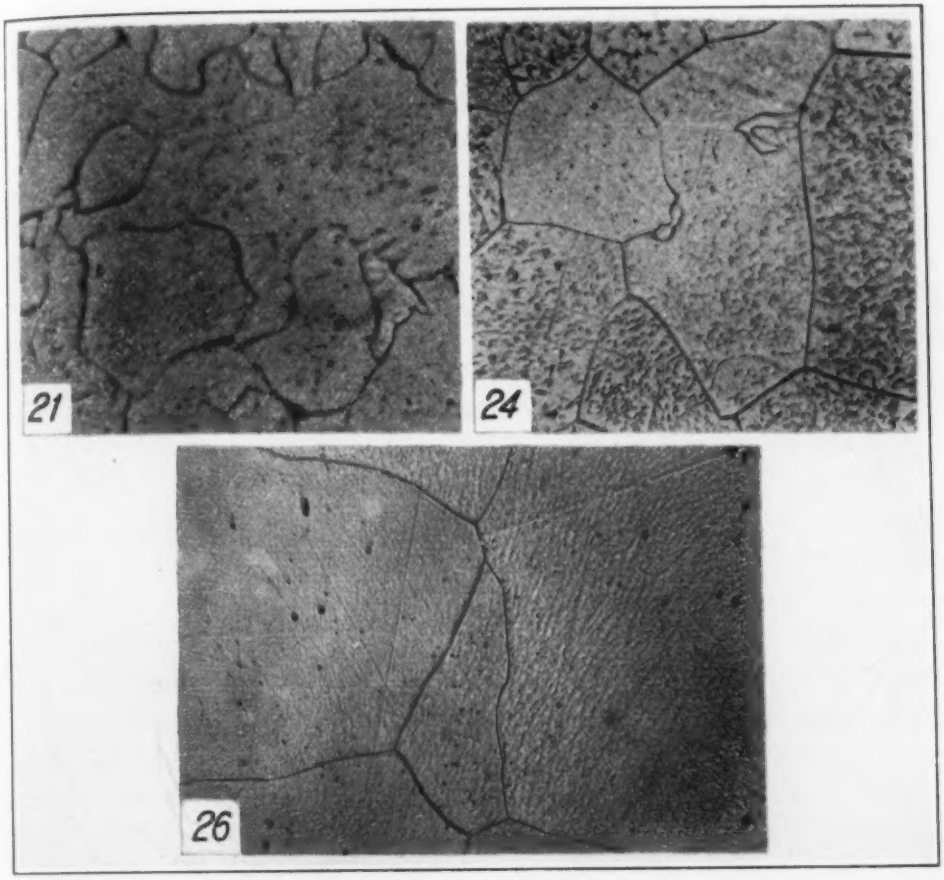

Fig. 21—Low Carbon Steel Quenched at 950 Degrees Cent., (1740 Degrees Fahr.) Drawn 4 Hours at 225 Degrees Cent. × 1500.

Fig. 24—Low Carbon Steel Quenched at 700 Degrees Cent., (1290 Degrees Fahr.) Drawn 24 Hours at 100 Degrees Cent. × 1500.

Fig. 26—Low Carbon Steel Heated 120 Hours in Hydrogen Between 925 and 950 Degrees Cent. (1700 and 1740 Degrees Fahr.). Quenched at 700 Degrees Cent., (1290 Degrees Fahr.) Drawn 4 Hours at 225 Degrees Cent. × 1000.

visible precipitate could be found. The results of these experiments are incorporated in Figs. 22 and 23, Curves B, C, and D. The general continuity of these curves, considered as a group, permit the following conclusions:

1. The particle size of the precipitated carbide is proportional to the temperature at which the precipitation occurs.
2. The hardening effect of the precipitated carbide is inversely proportional to the particle size (or to the precipitating temperature).

The tendancy of the precipitated carbide to migrate to the grain boundaries also undoubtedly plays a part in the above results, since this tendency would be allowed freer play at the higher temperatures.

Effect of Duration of Accelerated Aging

The effects of aging at five different temperatures (12, 55, 80, 100, 225 degrees Cent.) have been described above. It has been noted that the treatments at 100 and 225 degrees Cent. produce a visible precipitate of carbides and that their effects upon the mechanical properties of the steel are very similar. On the other hand, the treatments at 12, 55 and 80 degrees Cent. produce no visible precipitate and bring about much greater changes in the mechanical properties than do the draws at 100 and 225 degrees Cent. The aging temperatures are thus naturally divided into two groups according to the production or nonproduction of visible precipitate.

Now, the formation of a crystalline precipitate in any medium is a progressive action, commencing with the union of eight, twelve, or some other comparatively small number of atoms or molecules, with the resulting formation of an elementary crystal which is, of course, submicroscopic in magnitude. Other atoms or molecules attach themselves to this elementary crystal until some point is reached at which an observer is able to say that the crystal is of "visible size." In order to demonstrate the continuity of the relationship between the particle size of the carbide precipitate and its effect upon the mechanical properties of the steel the following experiment was performed: a number of test bars of the extra soft basic Bessemer steel were quenched at 700 degrees Cent. and their hardness immediately determined. These bars were then drawn at 100 degrees Cent. during various periods of time between 7 minutes and 26 hours. The change in hardness, which was determined immediately after each draw, will be found plotted against drawing time in Fig. 25. Each test piece was examined under the microscope after each draw to determine whether or not a visible precipitate had formed. Below a draw of ten hours there was clearly none. Between ten hours and twenty hours the precipitate was of "doubtful visibility"—the author believes the significance of this term will be readily understood. After a draw of 26 hours the presence of a visible precipitate was indisputable. The continuity of the relationship between precipitate particle size and age-hardening is clearly demonstrated by this experiment. The same investigation was also carried out by means of tensile tests and essentially the same results obtained.

Relationship Between Carbon Content and Aging Power of Soft Steel

If the author's interpretation of the phenomenon of age-hardening in soft steel is correct, the metal should abruptly lose its aging power when its carbon concentration is decreased to a value less than the carbon concentration of the point H on the equilibrium diagram

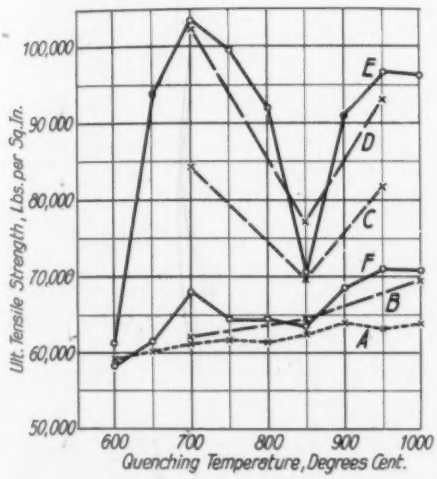

Fig. 22—Shows Results of the Draw at 225 Degrees Cent. (440 Degrees Fahr.). A—Results of Aging at 225 Degrees Cent. (440 Degrees Fahr.). B—Results of Aging at 100 Degrees Cent. (210 Degrees Fahr.). C—Results of Aging at 80 Degrees Cent. (175 Degrees Fahr.). D—Results of Aging at 55 Degrees Cent. (130 Degrees Fahr.). E—Results of Aging at 12 Degrees Cent. (25 Degrees Fahr.). F—Result of Quench.

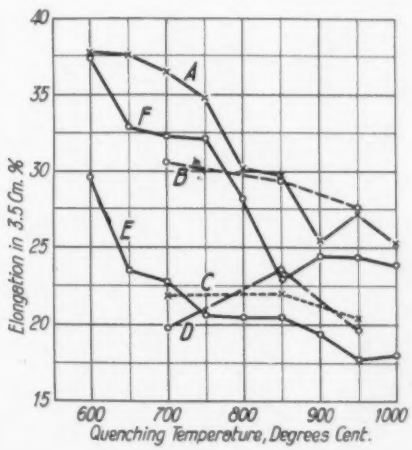

Fig. 23—Shows Results of the Draw at 225 Degrees Cent. (440 Degrees Fahr.). A—Results of Aging at 225 Degrees Cent. (440 Degrees Fahr.). B—Results of Aging at 100 Degrees Cent. (210 Degrees Fahr.). C—Results of Aging at 80 Degrees Cent. (175 Degrees Fahr.). D—Results of Aging at 55 Degrees Cent. (130 Degrees Fahr.). E—Results of Aging at 12 Degrees Cent. (25 Degrees Fahr.). F—Results of Quench.

(Fig. 7). Conversely, the determination of the carbon concentration at which soft steel loses its aging power should be a means of establishing the position of the point H.

To this end groups of bars of extra-soft basic Bessemer steel were decarburized during different periods of time in a stream of moist hydrogen at a temperature of 925-950 degrees Cent. This method of decarburization has been thoroughly investigated by Whiteley[3], Campbell[4, 5], Ross, Fink and others. It has been estab-

[3]Whiteley: *Journal,* Iron and Steel Institute, 1920, Vol. No. II, page 143.

[4]Campbell: *Journal,* Iron and Steel Institute, 1919, Vol. No. II, page 407.

[5]Campbell, Ross and Fink: *Journal,* Iron and Steel Institute, 1923, Vol. No. II, page 179.

Table III

Decarburization Hours in H at 950 Degrees Cent.	Carbon Concentration Per Cent	Free Fe_3C After Decarburizing Treatment	Free Fe_3C After Quench at 700 Degrees Cent.	Visible Ppt. After Quench and Draw at 225 Degrees Cent.
0	0.026	Yes	Yes	Yes
4	0.025	Yes	Yes	Yes
8	0.021	Yes	None	Yes
12	0.012	In scattered regions	None	In certain scattered regions
20	0.008	None	None	None
36	0.003	None	None	None
120	0.002	None	None	None
168	0.002	None	None	None

lished that by this treatment the oxygen and the phosphorus contents of the steel are changed only very superficially if at all. By means of chemical analysis the author has shown that no change oc-

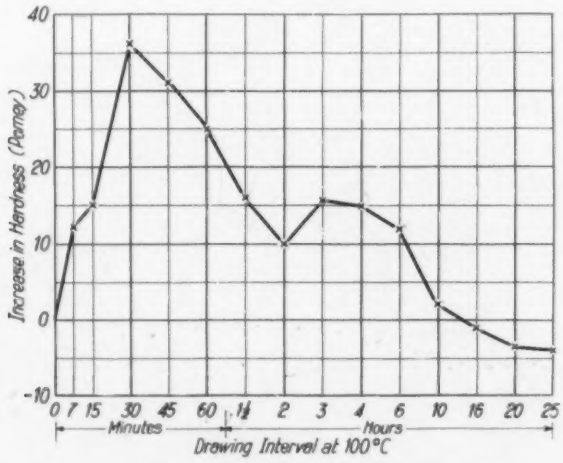

Fig. 25—Shows Change in Hardness as Determined Immediately After Each Draw as Plotted Against Drawing Time.

curred in the sulphur content. The carbon concentration of each group of decarburized bars was determined by attacking a 15-gram sample of the metal with oxygenated sulphochromic acid. The resulting CO_2 was precipitated as $BaCO_3$ and determined by titration[6] against standard HCl. Confirmation analyses were carried out on every group of bars by the ordinary combustion method using a 5-gram sample of the steel. The agreement between the two methods was generally within 0.002 per cent of carbon. The carbon contents

[6]For a complete discussion of this method of analysis see Travers, "Les Methodes de Dosage du Carbone dans les Fers, Fontes et Aciers". *Chimie et Industrie*, Vol. 7 Nos. 1-3, January-March 1922.

of the various groups of decarburized bars are given in Table III. In the same table are indicated the results of a metallographic study of each group. This study consisted: first, of a careful examination of each group immediately after the decarburizing treatment and again after a quench at 700 degrees Cent. in order to determine whether or not free Fe_3C was present; second, examination after

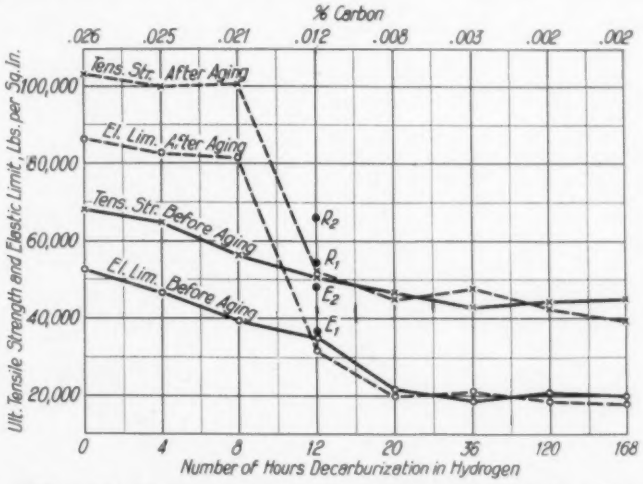

Fig. 27—Shows Determination of Respective Aging Powers of a Series of Low Carbon Steels. Six Bars of Each Analysis Quenched at 700 Degrees Cent. (1290 Degrees Fahr.). Three Bars Tested in Tension Immediately After the Quench and the Remaining Three Tested after a 60-Hour Draw at 55 Degrees Cent. (130 Degrees Fahr.).

quench at 700 degrees Cent. followed by a 4-hour draw at 225 degrees Cent. to determine whether the visible precipitate could be produced. It is assumed that the submicroscopic precipitate can occur only in those steels in which the visible precipitate can be produced.

It will be noted in the table that it was impossible to produce any precipitate in any steel containing less than 0.008 per cent of carbon. In Fig. 26 is shown a specimen of a bar containing 0.002 per cent carbon (5 days in hydrogen) which had been quenched at 700 degrees Cent. and drawn at 225 degrees Cent.

Having thus established the carbon concentration and the pertinent metallographic characteristics of a series of low carbon steels the author determined their respective aging powers by quenching six bars of each analysis at 700 degrees Cent., testing three of the bars in tension immediately after the quench, and testing the remaining three after a 60-hour draw at 55 degrees Cent. Fig. 27 shows graphically the results of this experiment.

Before drawing conclusions from this figure it is necessary to make an important comment. Careful microscopic investigation of all of the above steels had shown that decarburization in the case of the 20-hour treatment in hydrogen had left no trace of visible free cementite. From this it seems probable that the point H (Fig. 7) lies above 0.008 per cent carbon. On the other hand the decarburization in the case of the 12-hour treatment in hydrogen had been rather irregular so that, whereas in some portions of the bars there still remained particles of free carbide, other portions contained no trace of it. Furthermore, a subsequent anneal and re-examination after the bars had been broken, showed that fracture in every case had occurred in a carbide-free region. Now since the average carbon concentration of this steel was 0.012 per cent carbon, the fracture must have taken place in a region containing less than 0.012 per cent carbon. This argument, taken in conjunction with the fact that another group of bars, whose carbon concentration had been reduced to 0.012 per cent by a four-day heating in vacuum[7] at 850-875 degrees Cent., showed appreciable aging power seems to point to the conclusion that the minimum of carbon concentration necessary for age-hardening lies slightly below 0.012 per cent carbon. The steel which had been decarburized in vacuum also showed a slight amount of free carbide but this carbide was more evenly distributed than in the case of the 12-hour heat in hydrogen. It seems probable that the difference in the aging power of the two steels (each containing 0.012 per cent carbon) was due to this difference in regularity of carbon distribution. The tensile test results of the steel decarburized in vacuum are shown in Fig. 27 by the points:

E_1 = elastic limit after quench
E_2 = elastic limit after quench and aging at 55
R_1 = ultimate tensile strength after quench
R_2 = ult. tens. str. after quench and aging at 55

From the above argument it seems probable that the point H (Fig. 7) lies between 0.012 and 0.008 per cent of carbon.

General Conclusions

From the studies described in this article the following general conclusions may be drawn:

[7]The decarburization of very low carbon steel by long heating in vacuum at 850 degrees Cent. is probably due to the reaction $Fe_3C + 2FeO \rightleftarrows CO_2 + 5Fe$. This reaction is thermodynamically possible.

1. Low carbon steel is capable of age-hardening to a degree quite comparable with that found in duralumin and other aluminum alloys. This aging, suitably controlled, may bring about an increase of some 50 per cent or more in the ultimate tensile strength, elastic limit and Brinell hardness and, at the same time, a very considerable decrease in ductility and resilience.

2. The aging is principally due to a submicroscopic precipitate of carbides within the ferrite grains. The hardness conferred upon the steel by the precipitate is inversely proportional to the size of the individual particles of the precipitate.

3. The precipitation which requires about 25 or 30 days for completion at ordinary room temperatures, may be tremendously speeded up by heating the steel to comparatively low temperatures. Thus, 30 minutes at 100 degrees Cent. causes a very notable precipitation hardening.

4. The age-hardening may be entirely avoided by:

(a) a sufficiently slow cooling of the steel from temperatures near the A_1 point (720 degrees Cent.).

(b) a draw of suitable length of time at temperatures of 100 degrees Cent. and over (24 hours at 100 degrees Cent., 4 hours at 225 degrees Cent., etc.).

DISCUSSION

Written Discussion: By Yap, Chu-Phay, physical metallurgist and chemist, 27 Grove St., New York City.

After reading this paper several times, it struck me that Dr. Bates, if he were a biologist, would belong to the mechanistic rather than to the vitalistic school, because his explanation of age-hardening of very low-carbon steels is essentially mechanistic. It may be pure imagination, but I felt upon reading Dr. Bates' paper that it bears the impress of the French touch. For all that matters, this paper, in its bald logicality, its eclecticism and persuasiveness of style, reminds me of those interesting memoirs on the validity of the phlogiston theory, not that I wish to imply that Dr. Bates is defending a theory which he may be forced to abandon later. While I cannot go as far as to say that the paper under discussion has brought up anything revolutionary, nevertheless, it has distinction, which is more than I can say for many papers, and I wish to congratulate Dr. Bates without reservation for the interesting work he has done.

Several years ago I published my first paper under the highly misleading title of "Grain Growth in Mild Steels,"[1] in which I showed age-hardening in

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[1]Yap, Chu-Phay, "On Grain Growth in Mild Steels," TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 601.

mild steels containing about 0.10 per cent carbon. At 600 degrees Cent. (1110 degrees Fahr.) the maximum hardness, while small compared to that obtained by aging at room temperature, was reached only after 15 hours of annealing. Later when I was at Penn State, I persuaded a senior student to work on the problem, using Armco iron samples containing about 0.03 per cent carbon. I have been unable to date to get in touch with the proper party to ascertain his results. I recommended to him the use of the nitrobenzene solution originally suggested by Benedicks and later used by Pilling[2] because it darkens the carbide without, however, etching the grain-boundaries. I have personally found the solution to be quite delicate and wonder why it has not been used more in the study of carbides in steels. Although unimportant, I have certain doubts regarding the proper interpretation of Dr. Bates' photomicrographs Nos. 18, 19 and 20, to name but three.

In regard to his Constituent-X, it is, I think, only fair to call attention to

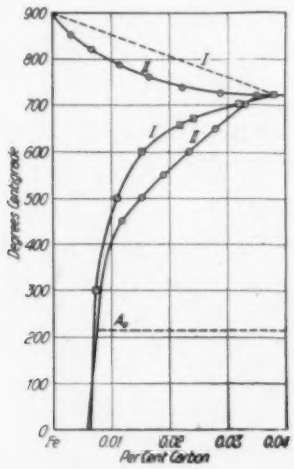

Fig. 1

the fact that Dr. John D. Gat[3] is apparently the first one to have discovered it metallographically. He thought that it is a ternary eutectoid of Fe-C-O, or more correctly, Fe-Fe_3C-FeO. I have already suggested elsewhere[4] the iron end of the Fe-O_2 constitutional diagram and it shows no eutectoid between Fe and FeO. The Constituent-X may be a supersaturated solid solution of FeO in α Fe or α Fe with FeO colloidally dispersed in it. There is, therefore, a need for the development of new etching reagents. Perhaps the Le Chatelier and Dupuy reagents are sensitive enough if properly used. I would recommend the adoption of Benedicks' method[5] of covering a polished sample with a thin

[2]N. B. Pilling, *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 70, 1924, p. 254.

[3]John D. Gat, "Normality of Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 376.

[4]Discussion of paper "Solubility of Oxygen in Solid Iron," by N. A. Ziegler, also being presented at this meeting.

[5]"Metallographic Researches," McGraw-Hill Book Co., New York, 1926.

film of collodion and then etching with a weak solution of $[Fe(CN)_6]$ K_4, which should color the Constituent-X in case it is a solid solution of FeO in α Fe.

In connection with my recent thermodynamics studies (to be published soon in the *Transactions* of the Faraday Society of London) I found that the A_{cm} line is theoretically merely a displaced Fe_3C solubility line in the melt. As this relationship holds in the case of austenite, it should hold also in such a dilute solution as α solid solution. In Fig. 1 of this discussion I show the solid solubility curve as derived from my thermodynamic studies, which may be compared to the one reported by Ehn[6] apparently on the basis of Masing's work. The agreement is as good as could be expected, especially in view of the experimental difficulties involved in determining the solid solubility line. On account of the numerous variables involved in such studies, one man's guess—and it is just as reasonable to assume that even actual experimental work is merely an attempt at approximation—is as good as another's and the writer prefers to make his guess on the basis of thermodynamic calculations.

Dr. Bates states that he has been unable to detect the presence of the precipitated carbide. I should like to suggest a simple method of indirectly showing the occurrence of this precipitation. After the sample has been carefully polished, hold it for a fraction of a second on the rougher wheel again so as to leave some scratches. Now, since aging is always accompanied by volume change and since no two grains are likely to be oriented alike, therefore, when precipitation occurs upon aging, the straight line across two or more grains will naturally show a displacement.

The length of this discussion should give Dr. Bates ample assurance of my interest in his work and we have every right to look forward to equally important contributions from him.

Written Discussion: By Felix F. Aloi, Seneca Iron and Steel Company, Buffalo.

The author has given one of the constituents encountered in this paper the name of "Constituent X," and he concludes as follows, "it is most unlikely that a pure austenite has been retained in the steel by the treatments which produced the Constituent-X." A few years ago during the quenching of a low carbon steel, S.A.E. 1010, we ran across the same constituent the author has termed Constituent-X, and in trying to determine what this constituent was, we took a piece of steel showing this constituent and heated it for five hours at 1100 degrees Fahr. and then examined it, we found that this Constituent-X had broken down into a sorbitic structure, so we concluded that the Constituent-X is a pure austenite retained after the quench. It seems that an austenite of definite carbon concentration is necessary to retain this pure austenite after the quench in low carbon steels.

Since the commercial low carbon extra deep drawing steel sheet has attained such a great importance in industry, especially the automobile industry, it is felt that it is worth while to discuss the aging or seasoning of this type of sheet steel, in connection with the conclusions stated in this paper. The author concludes that the age-hardening may be entirely avoided by:

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[6]E. W. Ehn, "Seasoning of Steel," *Metal Progress*, Vol. 20, September, 1930, p. 59.

(a) A sufficiently slow cooling of the steel from temperatures near the A point (720 degrees Cent.) (1330 degrees Fahr.).

(b) A draw of suitable length of time at temperatures of 100 degrees Cent. and over (24 hours at 100 degrees Cent., 4 hours at 225 degrees Cent., etc.).

From this conclusion we can say that the aging or seasoning found in commercial low carbon cold-rolled steel sheets is not caused by submicroscopic carbon precipitation, because in the usual manufacturing process of steel sheets, the process fulfills the above two statements. Therefore, the aging or seasoning of cold-rolled steel sheets by long periods of warehousing must be due to the slow "healing" of the slip planes after cold rolling.

Written Discussion: By H. M. Boylston, professor of mining and metallurgy, Case School of Applied Science, Cleveland.

Dr. Bates is to be congratulated on the work he has done in connection with the increase of tensile strength, hardness and brittleness in a very low carbon basic Bessemer steel after certain heat treatments and we must admire his brilliance in working out a theory concerning the cause of the unusual results obtained. Undoubtedly one of the reasons the subject has not been previously studied with very great care, at least in America, is because no basic Bessemer steel is made in this country and I have never heard of any being imported, so that the problem is of theoretical interest to steel makers.

There is one material made in this country which should respond to the treatment if the age-hardening theory of Bates is correct. I refer to Armco ingot iron of course, which has almost exactly the same carbon content (0.026 per cent or less) as the basic Bessemer steel used by Bates. The latter, however, has a very different manganese and phosphorus content, this being more in each case than ten times the contents of these two elements usually found in ingot iron, which has about 0.025 per cent manganese or less and not over 0.005 or 0.006 per cent phosphorus or even less. If the hardening effect is only the result of carbide being precipitated out of solid solution by the treatment, then Armco ingot iron should give similar results.

Until this point has been fully tested out, may we not feel that the question remains open as to the extent of the influence, if any, of manganese and phosphorus both of which are known to have an influence on the physical properties of iron of much the same type as carbon and phosphorus, both of these elements being present in the basic bessemer steel in much larger amounts (Mn, 0.34 per cent; P, 0.07 per cent) than is the carbon itself, and at least one of them, phosphorus, forming a phosphide with iron which dissolves in iron in solid solution when present in quantities up to 1.7 per cent phosphorus.

In spite of this possible doubt, we are all indebted to Dr. Bates for an important contribution to our knowledge of iron and I am very glad to welcome him back on my staff at Case this fall, after a year's leave of absence in France. Every effort will be made to encourage him to continue this research at our laboratories.

In his title Dr. Bates uses the word "aging" and this has come into rather common use as applied to some aluminum alloys and others. In the course of an attempt by the Joint Committee on Definitions of Heat Treatment terms to

define the term "aging" as applied to alloys of iron, it was pointed out to us (by Dr. J. A. Mathews) that there are two other operations used in treating steel which are known by the same name, namely, the aging (or stabilizing) of magnets and the aging of alloy steel bolts for high temperature service. In view of the difficulty which this situation creates, I suggest that hereafter we use the term "Age-hardening" for the phenomenon described by Bates and indeed this word is also used by Bates in the text of his paper and has been used by other writers also.

Written Discussion: By Ralph W. E. Leiter, research metallurgist, and Joseph Winlock, chief metallurgist, Edward G. Budd Mfg. Co., Philadelphia.

We have read the excellent paper by Dr. Bates with a great deal of interest. We agree with the author that aging as dealt with in this paper is caused by precipitation hardening but are not convinced that carbides are the sole agent. We should like to ask Dr. Bates if he has considered any effect that nitrogen might have in precipitation hardening. Nitrogen in steel has been studied quite extensively by many investigators and results seem to indicate that it is capable of precipitation hardening. The equilibrium diagram for iron-nitrogen is quite similar to that of iron-carbon and a 700-degree Cent. (1290 degrees Fahr.) quench would put most of the nitrides as well as carbides in solid solution.

Bessemer steel, due to the nature of the refining operation, generally runs fairly high in nitrogen. We would then expect this element to be playing a sizable rôle in the age-hardening described in this paper. In Fig. 25 change in hardness is plotted against drawing time at a temperature of 100 degrees Cent. A sharp maximum in hardness is shown after a 30-minute draw and is presumably caused by carbide precipitation of critical hardening size and number. This is followed by a rapid decrease up to the 2-hour draw. However, a curious increase in hardness is shown at the 3 and 4-hour draws. This second maximum in hardness suggests nitride precipitation. Nitride precipitation is considered[7] to be more sluggish than carbide precipitation and would thus require a longer time to develop critical hardening size and number at a given temperature. A study similar to the one in Fig. 25 with various drawing temperatures might be very valuable in giving accurate data on the relative rates of carbide and nitride precipitation.

Constituent-X discussed on page 457 is quite puzzling. It apparently has a definite relation to the free carbide areas that are to be found in the annealed samples. Constituent-X at 750 degrees Cent. (1380 degrees Fahr.), in our opinion, is austenite of fairly high carbon concentration. A sufficiently long anneal at that temperature should allow diffusion of the carbides and thus form 100 per cent solution alpha.

Written Discussion: By C. H. Herty, Jr., physical chemist, in charge of metallurgical section, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh.

This carefully thought out paper is an excellent illustration of the use of fundamental data in conjunction with experimental work. It would appear from this paper that all steels above 0.012 per cent carbon should show aging

[7] E. W. Ehn, "Seasoning of Steel," *Metal Progress*, Vol. 20, September, 1931, p. 59.

tendencies and those above about 0.03 per cent carbon should show aging tendencies regardless of quenching temperature. We would like to ask whether the author has done similar work on various steels between 0.06 and 0.10 per cent carbon.

Written Discussion: By Robert F. Mehl, assistant director, research laboratories, The American Rolling Mill Company, Middletown, Ohio, and Charles W. Briggs, metallurgist, Naval Research Laboratory, Washington, D. C.

In discussing Dr. Bates' paper, a brief review of the historical background might not be amiss, if Dr. Bates' contribution is to be viewed in proper perspective.

The first work which showed beyond doubt that this type of aging is like that in duralumin was that of G. I. Masing and L. Koch,[8] to which Dr. Bates referred. At the same time, and independently, W. Köster[9] studied the problem, much more in detail, and published a comprehensive paper of high excellence.

Köster pointed out that these new results had been partly anticipated by Welter[10] and by Ludwik and Scheu.[11] Masing, and Masing and Koch, studied three commercial steels, with 0.028, 0.044, and 0.120 per cent carbon. The first of these approximated very closely the composition of the steel studied by Dr. Bates. It was found that quenching from 660 and 700 degrees Cent. (1220 and 1290 degrees Fahr.), with subsequent retention at room temperature, or at slightly elevated temperatures, resulted in a very considerable increase in Brinell hardness number, from 60 to 90 points. In every case aging at room temperature gave a greater maximum hardness than at any elevated temperature, and at temperatures above 100 degrees Cent. resulted only in a softening. It was also observed that aging at room temperature increased the tensile strength by 21,000 pounds per square inch, and reduced the elongation from 12 to 13.5 per cent.

Köster studied these phenomena in great detail. He used eleven commercial steels, varying from 0.04 to 0.20 per cent carbon, and investigated the changes in tensile properties, notch-impact values, density, electrical conductivity, chemical attack by 1 per cent sulphuric acid, and magnetic properties. He found, in brief, that aging at room temperature following a quench from temperatures up to 680 degrees Cent. gave the maximum change after 14 days, and that during this time the yield point increased 62 per cent, the tensile strength 57 per cent, the Brinell hardness number 63 per cent, and that the elongation decreased 50 per cent and the reduction in area 14 per cent. Maximum hardness was obtained in aging at 50 degrees Cent., higher temperatures

[8]Masing and Koch's work originally appeared in complete form in Wissenschaftliche Veröffentlichung aus dem Siemens-Konzern, Vol. 6, 1927-28, p. 202 (Masing and Koch), and in *Archiv für das Eisenhüttenwesen*, Vol. 2, 1928, p. 185 (Masing).

[9]W. Köster, *Archiv für das Eisenhüttenwesen*, Vol. 2, 1929, p. 503; see also Köster discussion on Masing's paper, *Archiv für das Eisenhüttenwesen*, Vol. 2, 1927-28, p. 194; also *Stahl und Eisen als Werkstoff. Vorträge Werkstofftagung*, Berlin, 1927, Vol. III, page 16; *Zeit. für Metallkunde*, Vol. 22, 1930, p. 289.

[10]*Stahl und Eisen*, Vol. 43, 1923, p. 1347.

[11]*Ber. Werkstoffaussch. V. D. Eisenh.*, Vol. 70, 1925.

resulted in softening; the aging curves were entirely similar to those for duralumin for aging at room temperature and at elevated temperatures.

Köster found that even rapid air cooling was a sufficiently drastic quench to endow the steel with some aging capacity, and pointed out that this fact is of some importance in industrial metallurgy. The effect of the aging on notch-impact value is similar to that for over-strain aging: the temperature of the rapid decrease, normally in iron and steel at about 0 degrees Cent., is increased.

The theory to account for these changes may now be taken to be very satisfactorily established. Masing originally pointed out that the types of behavior shown by steel on aging are exactly of the duralumin type of aging, and that the variation in solubility of Fe_3C in α iron with temperature gave the necessary condition. Köster advanced more direct proof, producing data on electrical conductivity which showed an increasing solubility of Fe_3C in α iron with increasing temperature; furthermore, he determined the solid solubility by the Eggertz method for combined carbon, and showed that on aging practically all the carbide precipitated at 250 degrees Cent., at which point steel showed maximum attack by acid. These data, together with the fact that the degree of aging increases progressively, starting at 400 up to 700 degrees Cent., which is near the A_1 point, indicated that carbon was the active agent in these steels, at least the chief active agent.

In extending his work, Köster found that the aging capacity was markedly dependent upon the carbon content. The maximum increase in hardness after 14 days retention at room temperature, following quenching from 680 degrees Cent., rose sharply with the first few hundredths per cent carbon, reaching a maximum of 83 per cent at 0.03 per cent carbon, varying somewhat irregularly around 60-70 per cent between 0.06 and 0.17 per cent carbon, and falling rapidly to nearly zero at 0.6 per cent carbon. Also, he found that a "Vergüten" treatment, consisting of a quench from above A_3 and an anneal at 680 degrees Cent. robbed the steel of all capacity to age, presumably by some critical state of the spheroidized cementite. He found also that the darkening of Fry's etching agent, which indicates finely divided precipitate in iron, indicates such a precipitate here also. In passing, it should be remarked that Sachs recently performed a somewhat similar study, using low-carbon welding rod.

Dr. Bates' work lends additional support to the preëminence of carbon in these phenomena. His curves in Fig. 1 extend quenching experiments up to 1000 degrees Cent., and thus are new data. The maximum effect comes at A_1, indicating the effect to be that of carbon. It is well to stress this point, for the comparable critical point in Fe-O alloys is very close to A_3, whereas in the Fe-N system, it is near 600 degrees Cent. In addition to this evidence, his demonstration that aging is possible only when carbon exceeds 0.010 per cent (slightly above the probable solid solubility at room temperature) is especially happy, and again points to carbon as the active agent. The exact carbon composition at which aging appears should, of course, be in the neighborhood of 0.006 to 0.008 per cent, the extent of solid solubility of carbon in α iron. Some experiments conducted at the Naval Research Laboratory with Armco iron (C = 0.012 per cent, S = 0.018 per cent, P = 0.002 per cent, Mn = 0.030 per cent,

Si = 0.002 per cent, N = 0.018 per cent) quenched from 700 degrees Cent., aged 60 hours at 55 degrees Cent., showed a very slight increase in tensile strength, 40,650 to 41,150 pounds per square inch, but an appreciable increase in Rockwell hardness, B scale, from 59.4 to 63.4. It is quite obvious that the effects of other elements on the aging activity of carbon may well be appreciable, so that hairs cannot be split over such differences.

Dr. Bates' statement that a hydrogen treatment at 925-950 degrees Cent. does not appreciably reduce the oxygen or sulphur content of the steel requires correction. The reduction of oxygen content by hydrogen has been noted by Ledebur,[12] Whiteley,[13] Rooney,[14] and Pfeil.[15]

Our own work has shown the rate of reduction of oxygen to be quite rapid, in fact, more rapid than that of carbon. This reduction of oxygen takes place over a wide temperature range; at 1150 to 1200 degrees Cent. a treatment of 48 hours reduced the oxygen content in the strip from 0.030 to 0.0011 per cent, —96.5 per cent; after 140 hours at this temperature no oxygen could be found.

Similarly with sulphur, Charpy and Bonnerat,[16] Schmitz,[17] and Campbell[18] all report extensive desulphurization, though Pfeil was unable to detect sulphur elimination. We have found that desulphurization takes place over a range of temperatures; at 1150-1200 degrees Cent., 48 hours in hydrogen, reduced the sulphur from 0.018 to 0.009 per cent,—50 per cent, and 140 hours to 0.002 per cent,—89 per cent. Nitrogen is also rapidly eliminated, 48 hours at 1150-1200 degrees Cent. reduced the nitrogen from 0.0018 to 0.0006 per cent, and 140 hours to 0.0004 per cent, a total reduction of 88 per cent. These data will be reported in full later.

Author's Closure

I deeply regret that the important work of W. Köster, cited by Messrs. Mehl and Briggs, was not available to me until after my own paper was in print. Familiarity with Köster's investigation would have saved me much time and labor. I hereby apologize for having seemingly neglected to give credit for work accomplished.

Messrs. Mehl and Briggs, in correcting my statement that treatment by hydrogen during a period of 4 to 20 hours at 925 to 950 degrees Cent. removes oxygen and sulphur only superficially, have cited their own work carried out for a period of 48 hours at 1150 to 1200 degrees Cent. I do not believe that this constitutes a correction. Whiteley's work, to which reference has been made by both Mehl and Briggs and myself, showed that, whereas elimination of

[12] *Stahl und Eisen* (1882), 1931.

[13] *Journal*, Iron Steel Institute, No. 2, 1920, p. 407.

[14] *Journal*, Iron Steel Institute, No. 2, 1924, p. 122.

[15] *Journal*, Iron Steel Institute, Vol. 118, 1928, p. 167.

[16] *Comptes Rendus*, Vol. 156, 1913, p. 394.

[17] *Stahl und Eisen*, Vol. 39, 1919, pp. 373, 406.

[18] *Journal*, Iron Steel Institute, No. 2, 1919, p. 407.

oxygen by hydrogen is very rapid at 1100 degrees Cent. and above, the reaction is extremely slow at temperatures below 1000 degrees Cent.

Dr. Herty, Professor Boylston and Mr. Yap have all suggested an extension of this investigation to include materials other than basic Bessemer steel. That work of extension is, as a matter of fact, now under way. A year ago I carried out a few experiments on each of the following materials with results as here noted:

1. Electrolytic iron (carbon 0.02 per cent) showed a marked age-hardening after quench at 700 degrees Cent.
2. Armco iron (made in France) showed only slight age-hardening after quench at 700 degrees Cent. and considerable age-hardening after quench at 900 degrees Cent.
3. Three basic open-hearth steels containing respectively 0.12, 0.30 and 0.50 per cent carbon, when quenched at 700 degrees Cent. and aged, showed that ability to age-harden decreases rapidly as carbon content increases. The capacity for aging apparently disappears when the carbon concentration reaches about 0.60 per cent.

In answer to Prof. Boylston I can say at the present time only this, that Armco ingot iron can be age-hardened but that the relationship between quenching temperature and capacity for aging does not seem to follow the same curve as in the case of the basic Bessemer steel. It is quite possible, as Prof. Boylston suggests, that the manganese and phosphorus in the materials are responsible for this difference in aging properties.

In answer to Messrs. Leiter and Winlock I must say that I do not believe that nitrogen has played an important role in the work outlined in my paper. As Mehl and Briggs have pointed out in their discussion, the maximum solubility of nitrogen in iron occurs at about 600 degrees Cent. After a quench at that temperature the steel which I studied showed only a slight capacity for age-hardening. Furthermore, according to Ehn, a draw at 250 degrees Cent. does not materially decrease the hardness of nitrogen-hardened steel. In the basic Bessemer steel under discussion in this paper, a draw at 225 degrees Cent. completely removed all effects of age-hardening.

With regard to the phase which I have called Constituent-X, (here I refer to the suggestions of Messrs. Leiter, Winlock, Yap and Aloi), I do not believe that these crystals are pure austenite in exactly the sense in which that term is commonly understood. Whether or not oxygen enters into the composition of Constituent-X, it is certain that iron and carbon do. Fig. 19 shows the same effect discovered by Mr. Aloi, namely that Constituent-X breaks down to sorbite on heating to 200 degrees Cent. Actually this breaking down occurs at 100 degrees Cent. Evidently the constituent is highly supersaturated with respect to carbon. I do not believe that Constituent-X is the same as that discovered by Mr. Gat, as has been proposed by Mr. Yap.

I am quite ready to agree with Yap's opinion that my explanation of age-hardening is mechanistic. I am also very ready to believe that it does not by any means represent the final word in the matter. The form of the solubility curve of carbide in alpha iron as proposed by Yap is very interesting, as, indeed,

all of his thermodynamic studies have been. His newly proposed curve does not, of course, demand any essential modification in the explanation of age-hardening as advanced in this paper.

I hesitate to agree at this time with Mr. Felix Aloi in his contention that carbide precipitation can have nothing to do with the seasoning of low carbon cold-rolled sheet. We know little or nothing of the alterations in this type of precipitation which may be occasioned by variations in concentrations of other elements such as manganese, silicon, phosphorus, etc. Furthermore, from several experiments which I carried out subsequent to the printing of this paper, it seems probable that grain distortion due to cold work facilitates carbide precipitation. Several other investigators have come to a similar conclusion.

I wish to sincerely thank the gentlemen who have added interest to this paper by their comments and criticisms. Their many valuable suggestions will be kept in mind during the course of future investigations of age-hardening.

SHORT-TIME NITRIDING

By John J. Egan

Abstract

Several improved methods of nitriding are herein described, namely, the duplex cyanide treatment, the use of ammonia and nitric oxide, ammonia with nitrogen-containing compounds, and activated sand as packing material. The use of an electric spark in the nitriding chamber, ultraviolet irradiation of the specimen during treatment, and high frequency heating are also discussed. These methods all result in appreciable cases in a much shorter period of time than is possible by the present methods.

A wear testing machine has been designed and a number of tests carried out. Nitrided chromium-vanadium steel running against Stellite without lubrication shows 50 per cent less wear than any other combination tried.

Introduction

THERE exist today countless applications for nitriding in the case hardening of small machine parts such as in typewriters, vacuum cleaners, sewing machines, etc., in which extreme surface hardness is essential for wear-resistance, while due to low unit stresses, depth of case is a secondary consideration. By the use of ammonia alone, as the nitriding process is generally carried out, it is not possible to produce an appreciable case thickness in less than ten to fifteen hours. Thus, it is not practicable to get more than one run per working day per furnace. For this reason many prospective users are reluctant to depart from older methods of hardening which, although possessing many disadvantages, at least permit speed in production.

To reduce the time of the nitriding cycle has been the aim of metallurgists since the inception of the process some ten years ago. Two methods developed in the laboratories with which the writer is

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A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, John J. Egan, is a member of the society and is associated with the Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y. Manuscript received June 15, 1931.

associated have already been described before this society[1, 2]. These consist in the use of inert materials as packing in the usual ammonia treatment, and in the use of a special molten salt bath.

In the present paper, improvements in these methods are described as well as several other means of accomplishing this acceleration of the nitriding reaction. Although in some instances experimental work has not advanced beyond the laboratory stage, commercial possibilities are indicated and it has been thought advisable to present the results at this time when interest is high and research in the field so extensive.

Analyses of Steel Used

In general, the work described was carried out on two types of steel, a chromium-vanadium steel known to the trade as Nitralloy 630, and a chromium-aluminum steel known as Nitralloy 125. The analyses are given below:

	Nitralloy 630	Nitralloy 125
Carbon	0.25%	0.26%
Chromium	1.69	1.69
Vanadium	0.63	nil
Aluminum	nil	0.91
Molybdenum	nil	0.10

Evaluation of the Case

The testing of such thin cases as are here reported presents a difficult problem. Most instruments recognized at present as capable of measuring hardnesses of the order of nitrided steel are of the indenting type, the hardness number being a function of depth of penetration or some dimension of the impression produced under a given load. When working with these thin cases the penetrating medium easily breaks through, the reading thus becoming an integrated value of case and core hardness. Nevertheless, for purposes of comparison, all pieces here described were subjected to test in the Monotron and Rockwell "B", after which the case depth was measured under the microscope, using the etch developed by J. R. Vilella[2].

[1] A. B. Kinzel and J. J. Egan, "Nitriding Symposium," Transactions, American Society for Steel Treating, 1929, p. 175.

[2] A. B. Kinzel and J. J. Egan, Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 459.

The hardness of the cases reported was found to be of the same order as that of cases obtained by the usual long-time ammonia treatment, nominally 1000 Brinell. Due to difficulties in evaluating these thin cases (a condition encountered even with the deeper ones) any more quantitative statement has been avoided. Obviously the only true test is a service test, and in order to simulate service conditions many of the specimens were subjected to wear tests in a machine described later in this paper. These showed a wear-resistance equal to that of specimens nitrided by the usual methods for considerably longer periods. In most of the tests a treatment of four hours was adopted as standard. Although ten hours are required with the usual ammonia process all the methods here described produced appreciable cases with satisfactory hardness in four hours. For purposes of comparison the results of a four-hour treatment with ammonia alone are shown in Figs. 1 and 2.

The Duplex Cyanide Process

In the cyanide process, as originally reported, the work was heated for a period of two hours in a molten mixture of 47 per cent potassium and 53 per cent sodium cyanides. By this treatment cases of approximately 0.0005 inch depth were obtained, which, despite their thinness, possessed high surface hardness and wear-resistance.

The advantages of a molten bath as the nitriding medium are quite obvious. No preliminary flushing or subsequent cooling cycle is necessary, with their resulting loss of time, and the furnaces and other equipment are not tied up. On the other hand, the very thin cases obtained were a serious handicap, and considerable work has since been done in an effort so to modify the procedure as to bring about improved properties permitting wider commercial application.

Experiments having shown that, for a given time, case depth increased with the temperature, a combination of high and low temperature treatment was tried. Specimens were heated for two hours at 1200 degrees Fahr. (650 degrees Cent.) followed by two hours at 860 degrees Fahr. (460 degrees Cent.), resulting in a marked improvement in depth, but somewhat inferior hardness. Further work showed that successive 2-hour treatments at 1025 and 860 degrees Fahr. (550 and 460 degrees Cent.) for chromium-vanadium, and 1200 and 950 degrees Fahr. (650 and 510 degrees Cent.) for aluminum-bearing steel resulted in the most satisfactory properties.

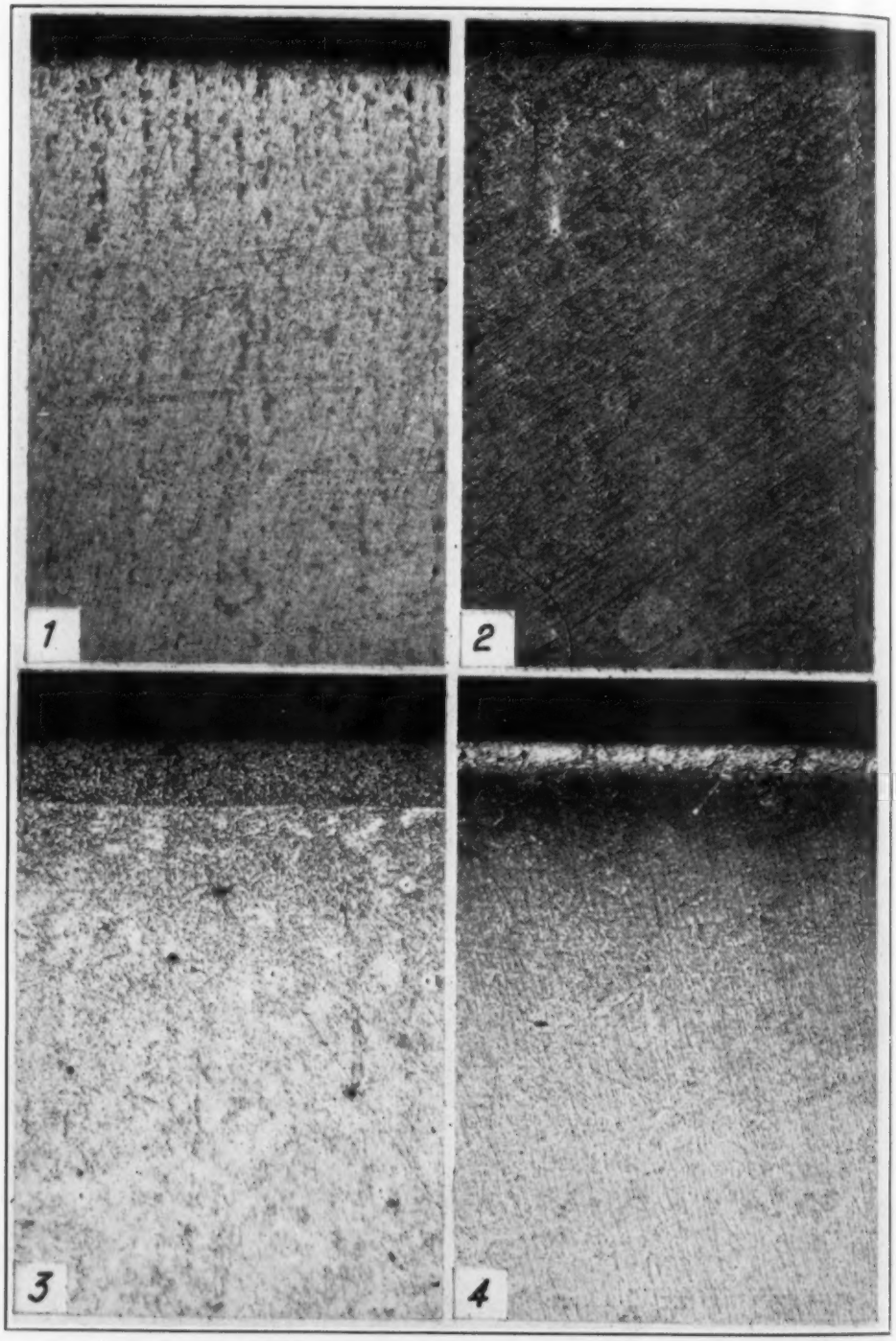

Fig. 1—Chromium-Vanadium Steel Nitrided 4 Hours at 860 Degrees Fahr., in Ammonia.
Fig. 2—Chromium-Aluminum Steel Nitrided 4 Hours at 860 Degrees Fahr., in Ammonia.
Fig. 3—Chromium-Vanadium Steel Nitrided in Cyanide Bath, 2 Hours at 1025 Degrees Fahr., 2 Hours at 860 Degrees Fahr.
Fig. 4—Chromium-Aluminum Steel Nitrided in Cyanide Bath, 2 Hours at 1200 Degrees Fahr., 2 Hours at 950 Degrees Fahr. All photomicrographs × 100.

Typical cases are illustrated in Figs. 3 and 4. The hardness was quite equal to the best obtained with the single low-temperature treatment and the case depths were increased to 0.004-0.005 inch. No differences were noted whether the duplex cycle was carried out in separate furnaces, the work being transferred from one to the other, or the furnace temperature lowered for the second treatment, the work remaining in the bath.

Several successful commercial applications of the process have already been made, of which the hardening of engraved master rolls for cloth printing is an excellent example. Here deep nitrided cases fail completely, due to brittleness, while the thin and considerably more ductile cases such as are produced in the cyanide bath outlast the best hardened steel rolls many times.

Mixtures of Ammonia and the Oxides of Nitrogen

In a search for more efficient gaseous nitriding media a study was made of those reactions or decompositions which at nitriding temperatures liberate nitrogen as one of their products. Among these the reactions between ammonia and the oxides of nitrogen seemed to hold particular promise. Baxter and Hickey[3] have reported that mixtures of ammonia and nitric oxide when passed over heated copper gauze or platinized asbestos react according to the following equation:

$$6NO + 4NH_3 = 5N_2 + 6H_2O$$

Nitrous oxide behaves similarly but with explosive violence. Tests were carried out in which a mixture of ammonia and nitric oxide was passed into the nitriding container, the nitric oxide being produced by the action of a solution of potassium nitrite on one of ferrous sulphate in sulphuric acid. After even as short a period as 2½ hours appreciable cases were found. Further tests in which the specimens were wrapped in copper gauze resulted in deeper cases. Later experiments seemed to indicate that as the amount of nitric oxide increased and approached the theoretical 60 per cent called for in the reaction, case properties were improved. Nitric oxide alone had no effect. Complete data, together with photomicrographs of typical cases are given in Table I and Fig. 5. Although the steel of the container or of the specimens seems to act to some extent as

[3] G. P. Baxter and C. H. Hickey, *American Chemical Journal*, Vol. 33, 1905, p. 300. (Abstract, *Journal*, Society of Chemical Industry, Vol. 24, 1905, p. 441.)

Table I
Specimens Nitrided at 860° F. with Mixture of Ammonia and Nitric Oxide

Steel	Time Hours	Remarks	Case Depth Inches
Cr-V	4	Specimen wrapped in copper gauze.	0.009
Cr-Al	2	Specimen wrapped in copper gauze.	0.004
Cr-V	2½	Specimen not wrapped in copper gauze.	0.003
Cr-Al	2½	Specimen not wrapped in copper gauze.	0.003
Cr-V	4	Specimen not wrapped in copper gauze.	0.005
Cr-Al	4	Specimen not wrapped in copper gauze.	0.004

Table II
Specimens Nitrided at 860° F. in Ammonia Passed Through Nitrogen-Containing Compounds at 212° F.

Steel	Time Hours	Remarks	Case Depth Inches
Cr-Al	4	Ammonia through Aniline	0.003
Cr-V	4	Ammonia through Aniline	0.007
Cr-Al	4	Ammonia through Nitrobenzene	0.003
Cr-V	4	Ammonia through Nitrobenzene	0.006
Cr-Al	4	Ammonia through Pyridine	0.002
Cr-V	4	Ammonia through Pyridine	0.004
Cr-Al	4	Ammonia through Alpha-Naphthylamine	0.002
Cr-V	4	Ammonia through Alpha-Naphthylamine	0.003
Cr-Al	4	Ammonia through Phenylene-diamine	0.002
Cr-V	4	Ammonia through Phenylene-diamine	0.003
Cr-Al	4	Ammonia through Quinoline	0.003
Cr-V	4	Ammonia through Quinoline	0.002
Cr-Al	4	Ammonia through Diethylamine (33%)	0.001
Cr-V	4	Ammonia through Diethylamine (33%)	0.001

a catalyst for the reaction, the best results are obtained in the presence of copper gauze or chips. Water vapor is one of the products of the reaction, but tests have shown that while a slight surface discoloration occurs the hardness of the case is not affected.

Ammonia Through Nitrogen-Containing Compounds

Some of the earlier investigators had reported that improvements in case properties were obtained when the ammonia was passed through benzol before entering the nitriding chamber. Considerable experimental work along this line was carried out at the author's laboratories and it was found that by the use of a nitrogen-containing compound, such as aniline, considerable improvement was effected. When the ammonia was passed through aniline heated in a water bath to 212 degrees Fahr. cases of approximately 0.007 inch on test pieces of chromium-vanadium steel and 0.003 inch on chromium-aluminum steel were obtained in four hours at 860 degrees Fahr. as shown in Figs. 6 and 7. A number of other compounds were

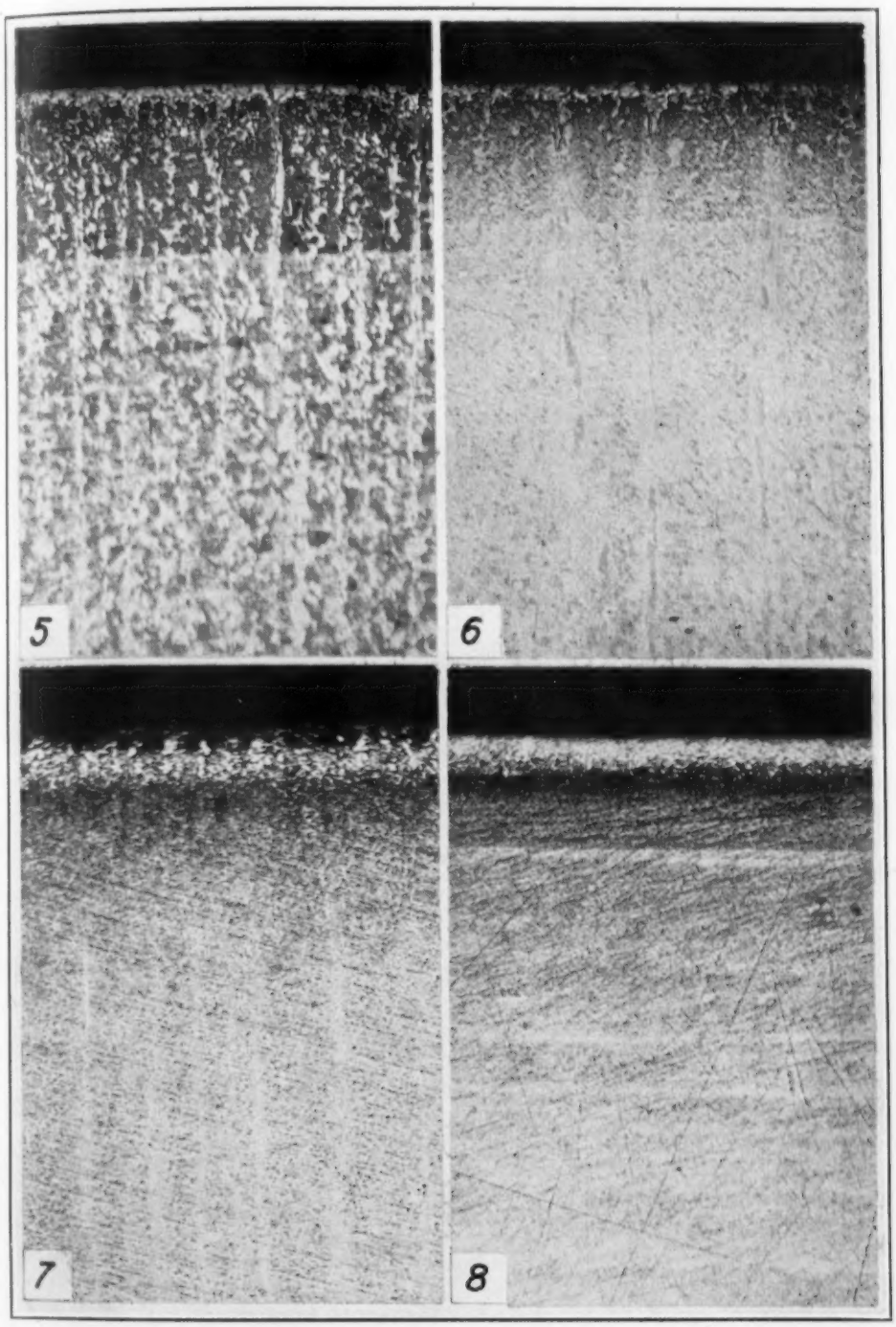

Fig. 5—Chromium-Vanadium Steel Nitrided 4 Hours at 860 Degrees Fahr., in Mixture of Ammonia and Nitric Oxide.

Fig. 6—Chromium-Vanadium Steel Nitrided 4 Hours at 860 Degrees Fahr. in Ammonia Bubbled Through Aniline at 212 Degrees Fahr.

Fig. 7—Chromium-Aluminum Steel Nitrided 4 Hours at 860 Degrees Fahr., in Ammonia Bubbled Through Aniline at 212 Degrees Fahr.

Fig. 8—Chromium-Vanadium Steel Nitrided 4 Hours at 860 Degrees Fahr., in Ammonia with Activated Sand as Packing Material. All photomicrographs × 100.

tried with very satisfactory results, e. g., quinoline, pyridine, alpha-naphthylamine, phenylene-diamine, and diethylamine. Full data are contained in Table II.

The greater efficiency of the aniline than of the other materials studied is quite evident. No very plausible explanation of the mechanism of the reaction has been advanced since no relation could be found to exist between nitriding efficiency and physical or chemical properties. Again, little information is available on the pyrolysis of these organic compounds. The majority of them do not break down directly into their elements on heating but pass instead through a series of decomposition products. Their behavior might be radically altered by the presence of the ammonia, the dissociation of the latter being in turn also affected. It is quite evident that before an explanation can be made considerably more work of a fundamental nature will be required.

Activated Sand as Packing Material

P. G. Nutting[4] has reported that by the treatment of sea sand with hydrofluoric acid or molten potassium hydroxide at 660 degrees Fahr. for 1-2 minutes, followed by boiling in hydrochloric acid, washing and drying, the oil-adsorbing properties of the material are greatly enhanced. In view of the successful results obtained with inert material as packing it was thought advisable to test the possibilities of this activated sand in nitriding.

Table III
Specimens Nitrided at 860° F. in Ammonia with Activated Sea Sand as Packing

Steel	Time Hours	Remarks	Case Depth Inches
Cr-V	4		0.006

Several runs were made using a vitreosil tube as the nitriding container, specimens of chromium-vanadium steel being packed in the sand and heated for four hours at 860 degrees Fahr. (460 degrees Cent.); excellent cases resulted as shown in Table III and Fig. 8. Somewhat higher surface hardness was noted in these cases over others of equal depths obtained by different methods, and it is thought that the wider surface zone, as shown in the figure, is the

[4]P. G. Nutting, *Science*, Vol. 72, 1930, p. 243.

cause of the phenomenon. This layer which probably represents the zone of highest nitrogen concentration is usually much narrower in cases produced by other means in the same period of time. The activated sand used was in the form of coarse particles of about 30 mesh, which should permit satisfactory heat conduction to the various parts of the container.

The Electric Spark

Dissociation measurements made during tests in which inert material was used as packing resulted in values considerably in excess of the customary 25-30 per cent. In spite of this, as previously reported, excellent cases were obtained, which suggested the possibility that this low dissociation was not essential to successful nitriding and various means of increasing it were accordingly investigated. A spark gap suitably mounted within the nitriding chamber and connected to an outside power source seemed a rather simple means of insuring high dissociation in the immediate vicinity of the work, and the apparatus shown in Fig. 9 was constructed. The electrodes consisted of $\frac{1}{16}$ inch iron wire, mounted in rubber stoppers so that the length and location of the spark with reference to the test piece could be varied. The usual induction coil circuit was used.

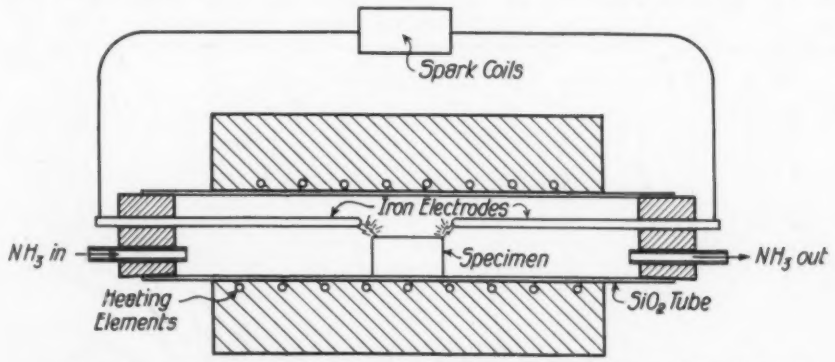

Fig. 9—Apparatus for Insuring High Dissociation in Immediate Vicinity of Work (Spark Gap Mounted Within Nitriding Chamber).

A preliminary test was made in which a specimen of chromium-aluminum steel was heated for four hours at 860 degrees Fahr. (460 degrees Cent.), the spark passing directly to the piece. Subsequent examination indicated a depth of 0.006 inch, as shown in Fig. 12. Further study indicated that best results were obtained when the spark was close to or directly upon the specimen. The next efforts were directed toward the construction of a metal container,

Table IV
Specimens Nitrided at 860° F. in Ammonia with Spark in the Nitriding Chamber

Steel	Time Hours	Remarks	Case Depth Inch
Cr-Al	4	Container illustrated in Fig. 9	0.006
Cr-V	4	Container illustrated in Fig. 10 (2 plugs)	0.006
Cr-Al	4	Container illustrated in Fig. 10 (2 plugs)	0.003
Cr-V	4	Container illustrated in Fig. 10 (4 plugs)	0.003
Cr-Al	4	Container illustrated in Fig. 10 (4 plugs)	0.002

Table V
Specimens Nitrided at 860° F. in Ammonia Under Influence of Ultra-Violet Light

Steel	Time Hours	Remarks	Case Depth Inch
Cr-V	1		0.002
Cr-Al	1		0.002
Cr-V	2		0.006
Cr-Al	2		0.003
Cr-V	6		0.008
Cr-Al	6		0.003
Cr-V	12		0.011
Cr-Al	12		0.004

Table VI
Specimens Nitrided in Ammonia at 860° F. in Container Heated by High Frequency Current

Steel	Time Hours	Remarks	Case Depth Inch
Cr-Al	4		0.008
Cr-V	4		0.010

and various forms typified by Fig. 10 were tried out, the results of the tests being given in Table IV. These cases in no instance equalled those made in the vitreosil tube, which may be due to the fact that only in the latter tests did the spark pass directly to the specimen.

Ultra-Violet Light

The effect of ultra-violet light on ammonia has been discussed by many investigators who have reported that under its influence decomposition is rapid. To study its possibilities in nitriding, the furnace shown in Fig. 11 was constructed and a series of tests made, the results of which are given in Table V; Figs. 13 and 14 show

typical cases. The work is placed in the chamber about the quartz tube. Ultra-violet light, produced by a special quartz mercury-vapor lamp extending through this tube, thus irradiates the metal and gas

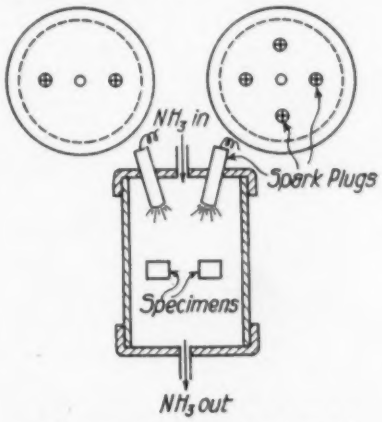

Fig. 10—Typical Metal Nitriding Containers with Spark Plugs Mounted Within.

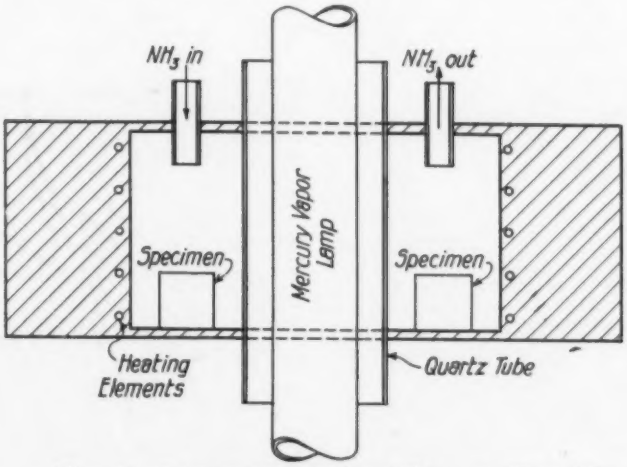

Fig. 11—Furnace for Testing Effects of Ultra-violet Light on Ammonia and its Possibilities in Nitriding.

during treatment. Dissociation under these conditions has been found to be quite high, which perhaps explains the ability to produce hard, satisfactory cases in a short time when ultra-violet light is used.

High Frequency Heating

In line with the general study of the possibilities of accelerating the nitriding reaction by means of irradiation and electric fields the action of high frequency currents was investigated. Many tests were made in which the nitriding container was heated in a high

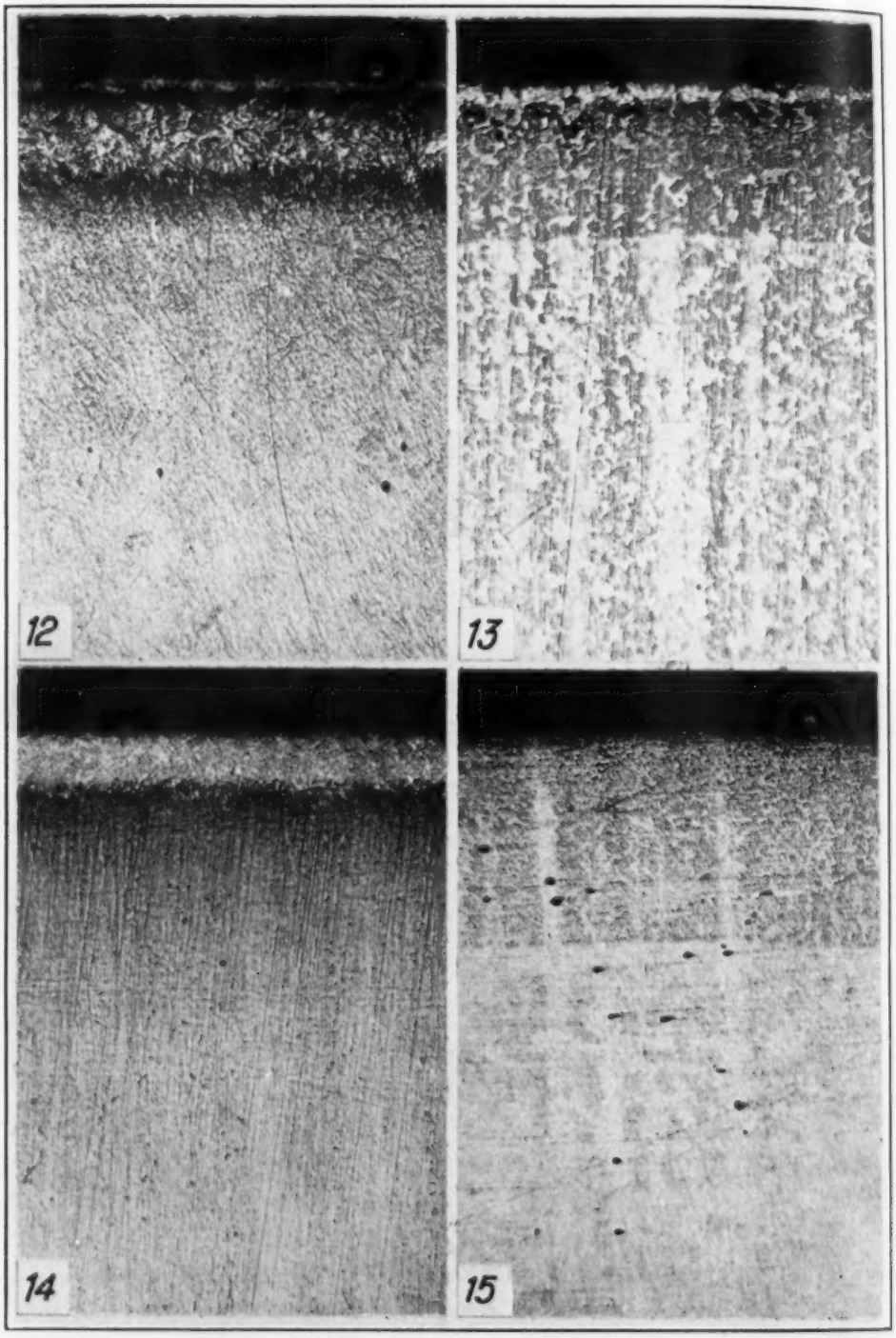

Fig. 12—Chromium-Aluminum Steel Nitrided 4 Hours at 860 Degrees Fahr., in Ammonia with Spark in the Nitriding Chamber. (See Fig. 9.)

Fig. 13—Chromium-Vanadium Steel Nitrided 6 Hours at 860 Degrees Fahr., in Ammonia Under Influence of Ultra-Violet Light. (See Fig. 11)

Fig. 14—Chromium-Aluminum Steel Nitrided 6 Hours at 860 Degrees Fahr., in Ammonia Under Influence of Ultra-Violet Light. (See Fig. 11)

Fig. 15—Chromium-Vanadium Steel Nitrided 4 Hours at 860 Degrees Fahr. in Ammonia. Container Heated by High Frequency Current. All photomicrographs × 100.

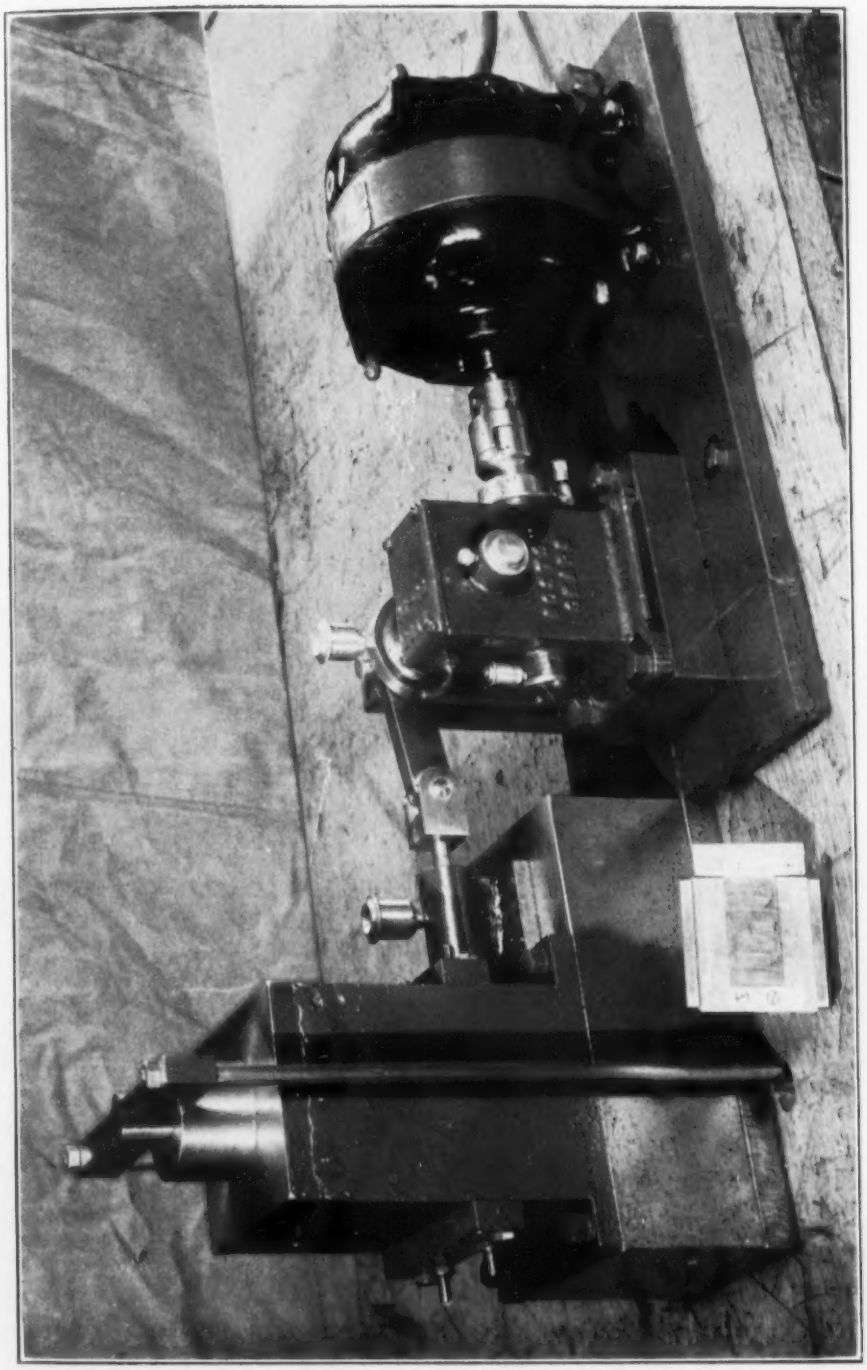

Fig. 16—Wear Testing Machine. (Side View)

frequency induction furnace. The results listed in Table VI show the remarkable improvement effected. A specimen of chromium-vanadium steel nitrided for four hours at 860 degrees Fahr. (460

degrees Cent.) is shown in Fig. 15. Mahoux[5] has recently reported a much increased nitriding speed when the specimen, during nitriding, is subjected to the action of high frequency oscillations, which substantially checks the work herein described.

Discussion

A study of the results of the tests brings out several interesting facts. Based on the efficiency of the methods, as measured by the depth of case produced in a given time, they may be broadly divided into two classes, the first group including the use of the ammonia-nitric oxide mixture, the electric spark, and the high frequency current heating; and the second, the duplex cyanide treatment, ultra-violet light, activated sand, and nitrogen-containing compounds. Of the more efficient processes, all included in the first group, the spark and the high frequency current require further study before they may be applied commercially. The use of the ammonia-nitric oxide mixture, on the other hand, should fit rather readily into routine nitriding since the method involves no great departure from current practice save the proper premixing of the gases and the use of the copper gauze or chips. In addition, the production of cases 0.01 inch in depth in four hours should insure its ready acceptance by the industry.

Wear Testing

Very early in the nitriding study conducted at these laboratories it became evident that some test was necessary to determine, approximately at least, the service potentialities of the cases. A wear testing machine was then constructed, as described in a previous paper[1], in which the specimen was rotated in a container of rusty water containing some grit, one end of the specimen passing through a stuffing box kept soaked with the water. While this was qualitatively satisfactory it did not permit any great variations in the wear conditions and the apparatus illustrated in Figs. 16 and 17 was therefore built. The machine is based on the design originally furnished by V. T. Malcolm, of the Chapman Valve Company, and consists essentially of two carefully aligned specimen holders, the upper one being held in place by means of set screws. Through a speed reducing and eccentric mechanism the lower holder describes a recip-

[5]G. Mahoux, *Comptes Rendus*, Vol. 191, 1930, p. 1328.

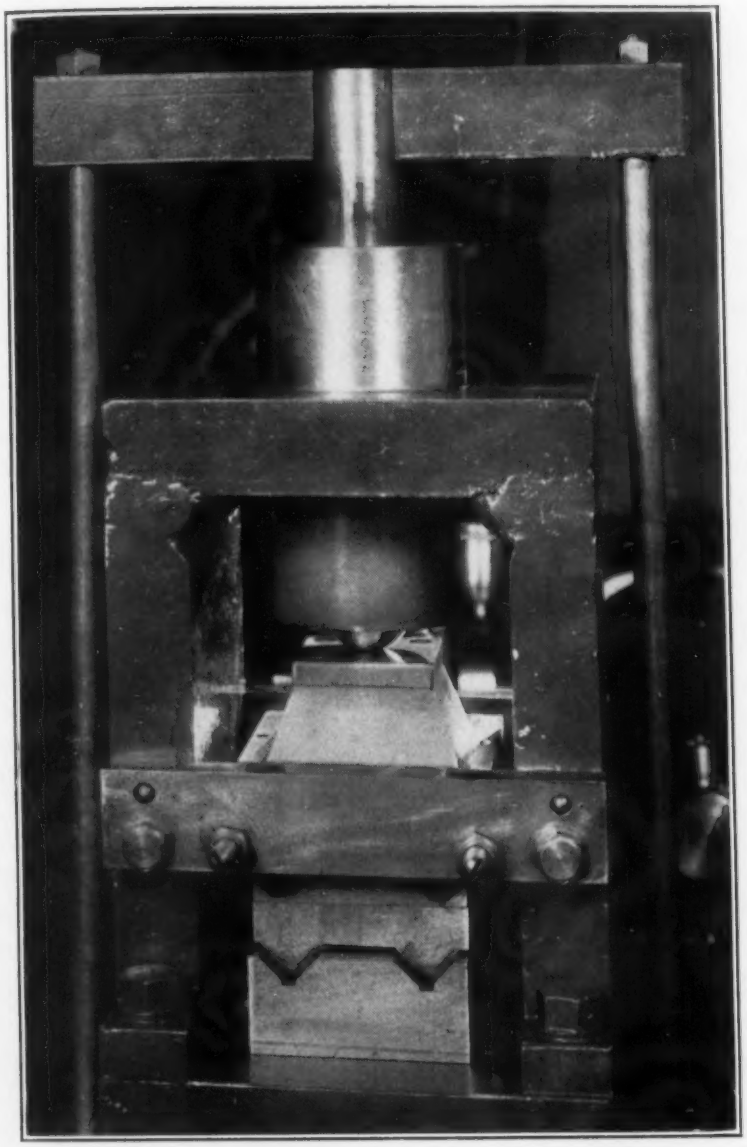

Fig. 17—Wear Testing Machine. (Front View)

rocating motion, moving through a stroke of two inches ninety times per minute. The specimens are thus caused to rub against each other, in perfect contact, under a constant load. This load is transmitted to the upper holder through the spherical-ended shaft shown in the photograph, the weights being hung below the machine. The specimens, which measure 1 x 2 x ¼ inch, are carefully ground to parallel faces before test and are weighed after each 10,000 strokes.

A number of tests have been made on various combinations of

metals under different loads, some of the results being given in Table VII. The thin cases described in this paper all gave satisfactory results, in some instances showing even greater resistance than the

Table VII
Weight Losses with Various Combinations
After 30,000 Strokes Under 10-lb. Load

Combination			Weight Loss
Nitrided Cr-V steel	vs	Stellite	0.0018 gram
Stellite	vs	Stellite	0.0041 gram
Nitrided Cr-V steel	vs	Nitrided Cr-Al steel	0.0053 gram
Cyanided Cr-V steel	vs	Hardened Tool Steel	0.0097 gram
Nitrided Cr-V steel	vs	Hardened Tool Steel	0.0193 gram
Nitrided Cr-Al steel	vs	Hardened Tool Steel	0.0239 gram
Hardened Tool steel	vs	Hardened Tool Steel	0.1312 gram

deeper ones. The pair showing the greatest wear-resistance was a special cobalt-chromium-carbon alloy and nitrided chromium-vanadium steel. An alloy known as Stellite No. 1 was thermally deposited on steel and then carefully ground to specimen size. The nitrided case was produced by a 50-hour ammonia treatment with magnesia packing, at 860 degrees Fahr. (460 degrees Cent.).

Acknowledgments

The author wishes at this time to thank the various members of the staff of the Union Carbide and Carbon Research Laboratories, Inc., who assisted in many ways in carrying out the various tests. He particularly wishes to acknowledge the many stimulating discussions and the helpful advice given by Dr. A. B. Kinzel, who was also responsible for initiating many of the experiments herein reported.

DISCUSSION

Written Discussion: By Samuel J. Rosenberg, associate metallurgist, Bureau of Standards, Washington, D. C.

While no criticism of the wear test results presented by Mr. Egan is intended, it is often misleading to place much faith in conclusions drawn from only a few wear tests. The results obtained from the first few tests of any pair of materials are so dependent upon such factors as the mechanical finish of the surfaces, alignment of the specimens in the testing machine, work-hardening of the wearing surfaces, formation of surface films, etc., that more frequently than not they are not at all indicative of the true wear-resistance of the materials tested. This is one point upon which investigators of wear are in general agree-

ment, namely, that conclusions drawn from the results of only a few wear tests are usually erroneous.

As an illustration of the case in question, the data in Fig. 1 (this discussion) are offered. These data represent the results of wear tests upon two grades of stellite. The tests were made in an Amsler wear testing machine under a load of 60 kilograms, which corresponds to a maximum pressure of

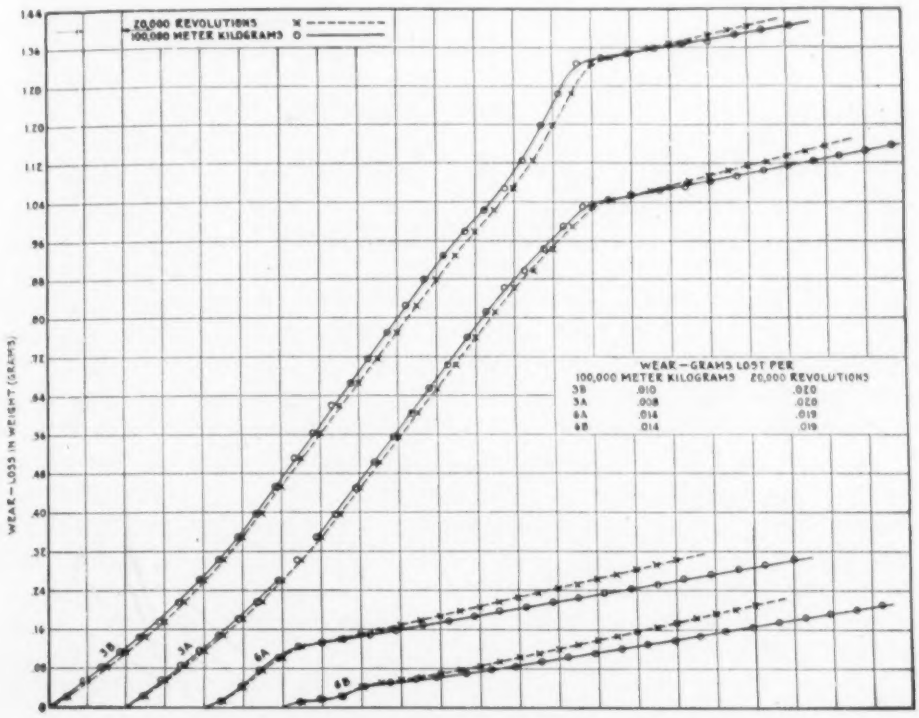

Fig. 1—Wear Tests of Two Grades of Stellite

about 74,000 pounds per square inch. The material against which the stellite was tested was a 0.81 per cent carbon steel heat treated to a hardness just under 60 on Rockwell "C" scale.

In tests of this type the loss in weight of the test specimen is usually plotted against the work consumed in friction between the specimens. When the curve assumes a definite slope, the wear per unit of work is calculated from this slope and this value is used as a measure of the wear. Had the losses in weights caused by the first three tests been added and used to express the wear, the weight losses of the specimens (after 30,000 revolutions) would have been as follows:

Grade 3	3 A	0.0862 grams
	3 B	0.0822 grams
Grade 6	6 A	0.0761 grams
	6 B	0.0236 grams

If these values are used as a measure of the wear, the duplicate specimens of grade 3 check very well, but the duplicate specimens of grade 6 give widely different results. If these results are averaged, they would show that the weight loss of grade 3 was almost twice as much as that of grade 6.

If the wear-resistance is based upon the weights lost over a longer period, comparisons may be made at the end of 24 tests, representing 240,000 revolutions. The weight losses are then as follows:

Grade 3	3 A	1.0294 grams
	3 B	1.0681 grams
Grade 6	6 A	0.3031 grams
	6 B	0.2106 grams

If these values are used as a measure of wear, the duplicate specimens of grade 3 again check very well while the duplicate specimens of grade 6 vary by about 50 per cent. If the averages are compared, these results would show that the weight loss of grade 3 was about four times that of grade 6.

When these four specimens are compared on the basis of weight lost per unit of work after the test specimens have definitely "worn in," the results shown in the figure are obtained. These individual values check quite well and show that despite the fact that the actual amount of weight lost by grade 3 was considerably greater than that lost by grade 6, the wear-resistance of grade 6 was only about two-thirds that of grade 3.

Written Discussion: By D. E. Ackerman, research laboratory, International Nickel Company, Inc., Bayonne, N. J.

I should like to secure Mr. Egan's views upon a few points pertaining to the wear test which he uses for estimating the utility of nitride cases.

It has been found in Amsler wear testing that the slope of cumulative weight-loss-time or cumulative weight-loss-work curves constitutes a much more satisfactory criterion of wear than the weight-loss after a given period of test. Mr. Egan's experience with data from his own wear machine seems to be rather different, and perhaps he will give us the benefit of his experience in the important matter of choosing a method of expressing wear test results. Would the order of merit of the nitride cases of Table VII have been the same if some other criterion of wear, such as the slope of the cumulative weight-loss-time curve, had been used? It would be of interest to know what degree of reproducibility Mr. Egan has been able to attain with his wear test.

I think Table VII could be profitably expanded to include the weight losses suffered by the individual specimens, in addition to those sustained by each pair of specimens.

During a visit to the Carbide and Carbon Laboratories some time ago, I noticed that films of red oxide, similar to those encountered in Amsler tests on ferrous materials in air, formed on the wearing surfaces of the nitrided specimens, although the unit stress here is only 5-10 pounds per square inch as compared with 10,000-100,000 pounds per square inch in the Amsler machine. I

should like to ask Mr. Egan what relation, if any, exists between the wear of a given pair of oxide filmed specimens and that of the same specimens when free from oxide. Does the presence or absence of an oxide film cause any difference in the relative weight loss of the individual specimens of any given pair?

Written Discussion: By V. O. Homerberg, associate professor of physical metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

Nitriding in a cyanide bath to procure a case depth of 0.004 to 0.005 inch in 4 hours with a surface hardness of 1000 Monotron-Brinell represents a very important accomplishment. There are a great many applications where this thickness of case is ample for the purpose.

In several instances the author has made comparisons in case depth between the chromium-vanadium and the chromium-aluminum-molybdenum steels after nitriding at 860 degrees Fahr. Such a comparison is not a fair one since this temperature is not the proper one to be used with the latter steel, although it is the most desirable one for the chromium-vanadium type. It is true, nevertheless, that vanadium tends to increase the depth of case.

Written Discussion: By Oscar E. Harder, assistant director Battelle Memorial Institute, Columbus, Ohio.

In connection with Mr. Egan's paper, in which he shows the effect of copper gauze on the depth of penetration, it is of some interest to note the results which have been obtained by nitriding copper-plated specimens.

British patent No. 345,659, granted to Sutton, Sidney, and Evans of the Royal Aircraft Establishment, provides for an alloy steel coated with copper, silver, platinum, arsenic, cobalt, or molybdenum, or any other suitable metal or metalloid, as a means of nitriding steels which are not satisfactorily hardened by the usual process. Specific mention is made of the following alloy steels:

No.	C	Cr	Ni	W	Mn	Mo
1	0.36	14.0	14.0	2.0	....	....
2	0.12	20.0	8.0	....	....	....
3	0.50	3.5	12.0	....	5.0	....
4	0.30	1.0	....	....	0.4	0.2
5	0.14	17.0	8.0	....	....	....
6	0.25	13.0	0.3	....	....	....
7	1.0	....	....	....	13.0	....

From results claimed in this patent, it would seem that copper either used as a gauze surrounding the material, as has been used by Egan, or as a coating, as has been used in the British patent, favors hardening by ammonia in the usual nitriding processes.

The findings of these two independent investigations seem to provide a very interesting coincidence and suggest further research on methods of catalyzing the nitriding reaction and on the mechanism of this reaction.

Oral Discussion

W. J. MERTEN:[1] In discussing Mr. Egan's excellent paper, and his new methods of nitriding, I want to particularly call attention to the fact that really his method of cyanide nitriding is a duplex process. His photographs show evi-

[1]Metallurgical Engineer, Lyon, Inc., Asbury Park, N. J.

dence to that effect, that he does carburize as well as nitride, and I believe the carburizing effect is accelerating the nitriding to the point where actually beneficial results from carburizing are obtained prior to nitriding. The temperatures of 1200 degrees Fahr. are sufficiently high to produce carburizing in liquid cyanide mixtures.

The idea of applying activated sand as a filler in the container is certainly unique, but certainly shows that a hunch may be helpful in development work. The electrolytic ionization in activating nitrogen has worked out equally well in experiments I have conducted. I consider this paper a very fine contribution to the nitriding art.

Author's Closure

I should like first to express my appreciation of the very interesting and pertinent discussion.

Replying to Mr. Rosenberg and Mr. Ackerman, I might say that we also realize that many difficulties are encountered in wear testing, and that unless great care is taken in the analysis of the final figures, misleading conclusions are quite likely to be drawn. The values given in Table VII are, however, representative of a number of tests performed by us, but inasmuch as the major subject of the paper was the presentation of some new nitriding methods it was not thought advisable to discuss wear testing at any great length. No difficulty was encountered in checking the order of magnitude of weight loss in various tests run under similar conditions. With regard to the question of the weight loss for a given number of strokes as against the slope of the weight-loss-time curve as a criterion of wear-resistance, inasmuch as weight losses are measured after every 10,000 strokes, the slope figures bear a direct mathematical relation to those representing weight loss. The effect on the test results of the so-called "red oxide film" which forms during a run cannot be measured, as it is not possible to subject two ferrous specimens to the test without the formation of this material.

Dr. Homerberg mentions the unfair comparisons between the chromium-aluminum-molybdenum and chromium-vanadium steels after nitriding at 860 degrees Fahr. No comparison at all was really intended. We desired to show that the nitriding methods described applied to all steels, and inasmuch as the greater volume of our work is done at 860 degrees Fahr. this was used in all cases.

We certainly agree with Dr. Harder that a very profitable line of research would lie in the study of the catalyzing and mechanism of the nitriding reaction.

In regard to Mr. Merten's discussion, as far as carburizing is concerned, we get very little if any carburizing in the short period and at the low temperatures used in the treatment. Tests which we have conducted on very thin specimens of steel which were analyzed after the treatment failed to show any increase in carbon, although they did show an increase in the nitrogen content.

THE COLD TREATMENT OF CERTAIN ALLOY STEELS

By G. V. Luerssen and O. V. Greene

Abstract

The paper points out the existence of certain alloys of the "borderline" type between the so-called austenitic and martensitic or pearlitic steels, showing that these alloys can be appreciably hardened by cooling to low temperatures. Studies are reported on several alloys including two chromium-nickel steels and two nickel-silicon steels, which are investigated in detail, and physical properties determined after such treatment. A detailed study is reported of a stainless steel containing approximately 17.50 per cent chromium and 5.00 per cent nickel capable of being hardened in solid CO_2 (dry ice), in which is included the determination of critical points. The practical application of such alloys is suggested since they may be hardened without discoloration of surface, developing unusual physical properties and corrosion resistance as well as improved machinability. A brief study is also reported upon high-nickel and high-nickel-molybdenum alloys.

Introduction

CONSIDERABLE data have been published in recent years upon the subject of austenite and the so-called austenitic steels. Work in this field has been due largely to the necessity of studying a number of commercial austenitic alloys, principally the non-corrosive chromium-nickel types and the Hadfield 12.00 per cent manganese steel. This work has resulted in the more or less arbitrary division of all steel alloys into two classes, first, the familiar class comprising the pearlitic and martensitic steels which are responsive to heat treatment, and which are magnetic in all conditions, and second, the less familiar class, the austenitic steels which are practically unchanged by heat treatment, remaining always virtually nonmagnetic. The first class is characterized by the well known critical points

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A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The authors are members of the society and are associated with the metallurgical laboratories of the Carpenter Steel Co., Reading, Pa. Manuscript received May 29, 1931.

occurring between room temperature and solidus line, making them susceptible to heat treatment. In the latter class of steels, however, it is popularly supposed that the added elements have either depressed the critical points considerably below atmospheric temperature, or have made the steel so sluggish that transformations are prevented at the usual temperatures. These steels are therefore characterized by the absence of critical points within the limits of temperature ordinarily attained, thus making them impossible to heat treat.

Between the two classes of steels just discussed, there must be a "borderline" class containing sufficient alloy to depress the transformation point below room temperature, yet not sufficient to prevent transformation if cooled to a sufficiently low temperature. Stated in practical terms, these alloys are capable of being hardened by the simple expedient of cooling to a low temperature, and since most of them are irreversible, having their A_c points in the vicinity of 600 degree Cent., (1110 degrees Fahr.), once hardened, they remain stable at ordinary temperatures. The investigation of the properties and behavior of this unique class of alloys affords a most fascinating study, not only in its academic aspects, but from a practical stand point as well, since there appears to be a rather potential field for their application, particularly in the case of those alloys possessing corrosion resisting properties.

It is the purpose of the present paper to report upon the determination of some of the more important characteristics of several of these alloys. It is hoped that these results will suggest further work to add to our store of knowledge, not only of this particular group of alloys, but of the more general problem of austenitic transformation.

Previous Work

The determination of critical points below room temperature and consequent hardening by supercooling is not new. As early as 1914 Chevenard[1] determined the A_r point in a 32 per cent nickel steel at —125 degrees Cent. (—193 degrees Fahr.) Broniewski[2] in 1920 patented a method based upon Osmond's earlier work, for super-

[1]Chevenard, *Revue de Metallurgie*, Vol. 11, 1914, p. 841. Also "Invar and Related Nickel Steels," U. S. Bureau of Standards, Circular No. 58, 1916, p. 35.

[2]Witold Broniewski, "Superficial Hardening of Certain Special Steels," French patent 503113, Patents March 9, 1920.

ficially hardening several austenitic steels by cooling rapidly to low temperatures. Mathews[3], Sykes and Jeffries[4], Harder and Dowdell[5] and Honda and Iwase[6] have all studied the transformation of retained austenite in tool steels by cooling in liquid oxygen.

Apparently, however, no large amount of systematic work has been done upon the determination of actual critical ranges, nor have any practical applications of cold treatment been made.

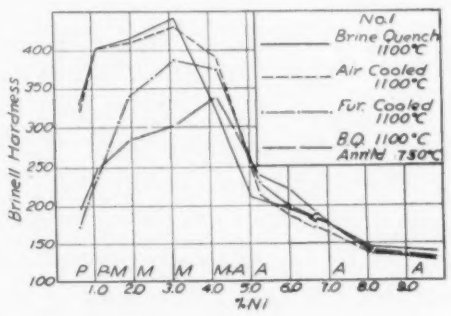


Fig. 1—Hardness and Structure of Steels Containing Approximately 17.50 Per Cent Chromium and Varying Amounts of Nickel Treated as Shown.

Physical Properties of the Chromium-Nickel Types

The most fruitful types for investigation in this field are steels containing approximately 0.10 per cent carbon, 18.00 per cent chromium, with nickel contents varying up to 8 per cent. This range comprises the steels patented by Benno Strauss. Fig. 1 shows graphically the hardness values and structures obtained upon a series of pieces approximately 1 inch in diameter, varying in nickel from 0.65 up to 9.75 per cent, after cooling at three different rates from 1100 degrees Cent., (2010 degrees Fahr.) and after brine quenching from 1100 degrees Cent., subsequently annealing at 750 degrees Cent. (1380 degrees Fahr.). It will be noted that up to a content of 4.00 per cent nickel, the steels are pearlitic or

[3]J. A. Mathews, "Decomposition of Retained Austenite," Transactions, American Society for Steel Treating, Vol. VIII, 1925, p. 565.

[4]W. P. Sykes and Zay Jeffries, "On the Constitution and Properties of Hardened Steel," Transactions, American Society for Steel Treating, Vol. 12, 1927, p. 871.

[5]O. E. Harder and R. L. Dowdell, "Decomposition of Austenite in Liquid Oxygen," Transactions, American Society for Steel Treating, Vol. 9, 1927, p. 391.

[6]Kotaro Honda and Keizo Iwase, "Decomposition of Austenite in Liquid Air," Transactions, American Society for Steel Treating, Vol. 9, 1927, p. 399.

martensitic, responding to heat treatment in the usual way. Above 5 per cent nickel, however, it is not possible to harden the alloys by any of the treatments noted, the resulting structure in every case being austenitic. The steels containing approximately 5 per cent nickel obviously represent the borderline alloys already referred to, viz., those having an A_r point slightly below atmospheric temperature. Series similar to this have already been published by Bain and Griffiths[7] and more recently by Krivobok and Grossmann[8].

The first attempts to determine the depressed A_r point were made by what will be hereafter termed the interrupted magnetic method. A test specimen 1 inch x ¼ inch in section by 10 inches in length, having an iron-constantan thermocouple welded to the middle, was cooled first in iced brine and then in solid CO_2, the first temperature reached being about —7 degrees Cent., and the second about —75 degrees Cent., (—103 degrees Fahr.) temperatures being recorded on a potentiometer. No effort was made to control the rate of cooling, which was rapid in every case. As each temperature was reached, the bar was quickly transferred from the low temperature pack to a Fahy permeameter, and a permeability reading immediately taken for a magnetizing force of 200 Gilberts per centimeter. With the bar still in the permeameter, additional permeability readings

Table I
Analyses of Chromium-Nickel Steels Used

Steel No.	In Per Cent C	Mn	Si	P	S	Cr	Ni
1	0.13	0.52	0.41	0.011	0.014	17.55	4.13
2	0.18	0.36	0.54	0.016	0.013	17.24	5.23
3	0.11	0.52	0.41	0.011	0.012	17.66	5.99
4	0.09	0.49	0.36	0.011	0.013	17.62	7.04
5	0.10	0.27	0.38	0.022	0.004	17.62	4.03
6	0.08	0.39	0.52	0.013	0.005	17.15	5.06
7	0.19	0.14	0.27	0.010	0.009	17.23	4.73
8	0.13	0.21	0.42	0.011	0.009	17.84	4.94
9	0.16	0.19	0.53	0.011	0.011	17.57	4.97
10	0.13	0.18	0.45	0.008	0.010	17.67	5.05
11	0.13	0.14	0.55	0.011	0.011	17.52	5.10
12	0.15	0.15	0.42	0.006	0.008	17.70	5.16
13	0.08	0.51	0.98	0.009	0.017	17.95	5.24
14	0.20	0.19	0.46	0.014	0.011	17.60	5.36
15	0.22	0.10	0.52	0.008	0.011	17.27	5.54
16	0.10	0.34	0.50	0.008	0.008	17.60	5.08
17	0.11	0.39	0.60	0.010	0.010	18.27	9.20

[7]E. C. Bain and W. E. Griffiths, "An Introduction to Iron-Nickel-Chromium Alloys," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 75, 1927, p. 166.

[8]V. N. Krivobok and M. A. Grossmann, "Influence of Nickel on the Chromium-Iron-Carbon Constitutional Diagram," TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 808.

were then taken at definite temperature intervals as the bar gradually heated to room temperature. Steels containing approximately 17.50 per cent chromium and 4.00, 5.00, 6.00 and 7.00 per cent nickel were tested in this manner, complete analyses of which are shown in Table I, Steels numbers 1, 2, 3 and 4. Briefly the results were as follows:

The 4.00, 5.00 and 6.00 per cent nickel steels all showed a steady and marked increase in permeability when cooled to successive tem-

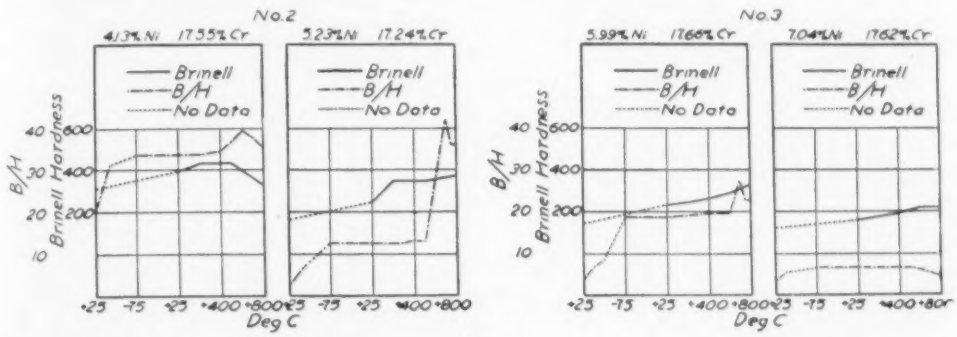


Fig. 2—Hardness and Permeability ($\frac{B}{H}$ for H = 200) of Four Steels of Different Nickel Content after Progressive Treatments.

peratures under atmospheric, and this permeability remained constant as the bar returned to room temperature, indicating that the transformation was "irreversible". Increases in permeability in every case were accompanied by increases in hardness. The 7.00 per cent nickel alloy showed no increase in permeability down to —75 degrees Cent., (—103 degrees Fahr.) with no noticeable increase in hardness.

To continue the experiment still further, the bars were next heated in increments of 100 degrees Cent. to temperatures up to 800 degrees Cent., (1470 degrees Fahr.) permeability and hardness determinations being taken after returning to room temperature in each case. Complete results on these four alloys, starting at room temperature, then going down to —75 degrees Cent., (—10 degrees Fahr.) returning to room temperature and going to the successive elevated temperatures, are shown graphically in Fig. 2.

It is obvious from the graphs that the 4.00 and 5.00 per cent nickel steels are the most responsive to cold treatment, and the possibility of obtaining a very appreciable pick-up in Brinell hardness by cold treatment, particularly in the 5.23 per cent nickel steel is at once apparent. It is interesting to note that the peak in the permeability curve is passed at about 600 degrees Cent., (1110 degrees Fahr.) which probably marks the A_c point.

Table II

Physical Properties of Steel No. 5 Containing 17.62% Cr-4.03% Ni After Treatments Shown

Quenched from 1090° C. (1995° F.) and cold treated —80° C. (—112° F.), and drawn

Treatment	Elastic Limit Zero P. L. Lbs. Per Sq. In.	Elastic Limit .0002" Off Lbs. Per Sq. In.	Ultimate Tensile Lbs. Per Sq. In.	Elong. in 2" %	Red. of Area %	Izod Values Ft. Lbs.	Machinability R.P.M.	Brinell No.	B_{max} H-300	Specific Volume
As Quenched	27,500	45,000	211,000	6.8	9.6	34–34	120	401	8740	.129102
C. T. —80° C.	42,500	65,000	207,400	3.7	5.8	29–31	120	418	10040	.129498
Draw 200° C.	60,000	85,000	203,000	10.3	19.2	64–65	120	401	10540	.129234
Draw 400° C.	87,500	122,000	209,900	17.4	64.1	46–46	120	435	10540	.129246
Draw 600° C.	47,500	60,000	140,000	19.7	57.5	64–67	160	278	9440	.129052
Draw 800° C.	33,100	43,300	174,000	15.4	55.9	16–13	160	330	11840	.129572
Quenched from 1090° C., and drawn, without cold treatment.										
Draw 400° C.	52,500	92,500	188,300	19.5	55.8	83–85	120	402	9600	.129232
Draw 500° C.	42,500	80,000	190,600	22.9	65.2	69–76	160	387	10000	.129264
Draw 600° C.	45,000	62,500	152,300	16.0	52.4	45–35	221	302	11800	.129529
As rolled and cold treated, and drawn.										
As rolled	37,500	52,500	141,400	1.8	3.5	30–24	120	402	7800	.128801
C. T. —80° C.	40,000	70,000	149,300	1.2	3.9	24–16	88	444	8300	.128962
Draw 400° C.	82,500	102,500	187,400	3.7	11.1	24–26	88	402	8800	.128869
Draw 500° C.	60,000	72,500	177,800	11.6	29.8	27–27	88	364	11900	.129382
Draw 600° C.	37,500	55,000	150,000	15.9	44.9	41–40	160	302	11100	.129177
As rolled and drawn, without cold treatment.										
Draw 400° C.	47,500	92,500	186,700	8.0	13.0	36–29	160	402	8700	.128809
Draw 500° C.	42,500	72,500	196,800	13.9	21.6	39–35	160	375	8800	.128745
Draw 600° C.	40,000	57,500	158,500	10.6	26.1	51–34	160	321	12600	.129401

The work up to this point therefore indicated the possibility of developing a stainless chromium-nickel steel of the austenitic type which could be changed from the austenitic to the martensitic state at will, and vice versa. The advantages to be gained in such an alloy would be, first, the possibility of hardening without scale or even discoloration, second, the possibility of changing the austenitic alloy into a partially martensitic or even troostitic condition so as to improve its machinability, later changing back to the austenitic condition if desired, and third, the ability to harden the austenitic alloy by a method which does not involve cold working as is usually practiced. With these general points in mind, a complete study of the physical properties was made of two analyses, one containing 4.03 per cent nickel and the other 5.06 per cent nickel, complete analyses of which are given in Table I, Steels 5 and 6.

Some of these were cold treated at —80 degrees Cent. (—112 degrees Fahr.) and drawn from the hot-rolled condition, while others were given a preliminary brine quench from 1090 degrees Cent. In both cases tests were made for comparison upon similar specimens not cold-treated. Cooling rate was maintained at about ten degrees centigrade per minute.

Table III

Physical Properties of Steel No. 6, Containing 17.15% Cr and 5.06% Ni After Treatments Shown

Treatment	Elastic Limit Zero P. L. Lbs. Per Sq. In.	Elastic Limit .0002" Off Lbs. Per Sq. In.	Ultimate Tensile Lbs. Per Sq. In.	Elong. in 2" %	Red. of Area %	Izod Values Ft. Lbs.	Machinability R.P.M.	Brinell No.	B_{max} H-300	Specific Volume
Quenched from 1090° C. (1995° F.) and cold treated at −80° C. (−112° F.), and drawn										
As quenched	20,000	22,500	194,500	17.0	22.6	91–93	120	277	3540	.127700
C. T. −80° C.	35,000	72,500	231,200	8.4	9.6	32–32	88	444	9240	.129171
Draw 400° C.	50,000	100,000	208,000	19.8	64.3	81–77	160	444	9970	.129040
Draw 500° C.	47,500	82,500	187,200	20.6	65.8	78–75	221	387	10940	.128709
Draw 600° C.	47,500	65,000	153,600	19.4	55.9	62–56	221	321	8270	.128805
Quenched from 1090° C. and Drawn, without Cold Treatment.										
Draw 400° C.	20,000	22,500	173,500	17.5	21.3	104–111	160	262	3370	.127563
Draw 500° C.	20,000	25,000	171,500	23.6	37.2	112–116	160	269	4040	.127893
Draw 600° C.	15,000	22,500	160,900	19.0	34.1	66–62	160	311	7240	.128437
As rolled and cold treated −80°C., and drawn.										
As rolled	22,500	32,500	141,800	5.1	7.7	30–29	120	293	2700	.127310
C. T. −80° C.	37,500	57,500	175,700	2.4	4.3	12–10	120	430	7040	.128443
Draw 400° C.	50,000	75,000	200,000	5.1	9.6	10–7	120	444	7840	.128545
Draw 500° C.	22,500	42,500	188,300	7.3	9.2	13–9	160	387	9540	.128652
Draw 600° C.	17,500	45,000	158,900	14.1	34.3	20–16	221	321	8500	.128819
As rolled and drawn, without cold treatment.										
Draw 400° C.	22,500	30,000	143,200	8.5	11.5	39–37	160	277	2700	.127130
Draw 500° C.	20,000	37,500	157,200	10.0	24.1	14–14	160	293	3240	.127400
Draw 600° C.	30,000	42,500	166,100	7.5	10.4	17–14	160	332	9240	.128773

Complete results of tests are shown in Tables II and III. The tensile specimens used were the standard 0.505 inch section, threaded end, treated in a 0.530 inch diameter section. Elastic limit was determined by the release load method, the "Zero P. L." figure being the highest stress possible without showing a set after release, and the "0.0002 off" figure being the highest stress possible without showing a stretch of more than 0.0002 inch in 2 inches. Izod tests were made upon square specimens, with a standard notch, and were broken on a 120-foot pound machine.

Machinability determinations were made as follows:

Specimens ½ inch round in each condition were set up in a lathe and machined with a ⅜ inch square high speed tool bit having a rake angle of 16 degrees and a face angle of 15 degrees, a side angle of 8 degrees and a radius of $\frac{1}{16}$ inch on the nose. Maximum lathe speeds permissible in revolutions per minute to produce a smooth finish on the specimen without undue wear or galling of the tool were recorded. The test length was 4 inches, the depth of cut was ⅛ inch on the diameter, and the cross feed 0.007 inches per revolution.

Brinell hardness determinations were made upon a flat, ground

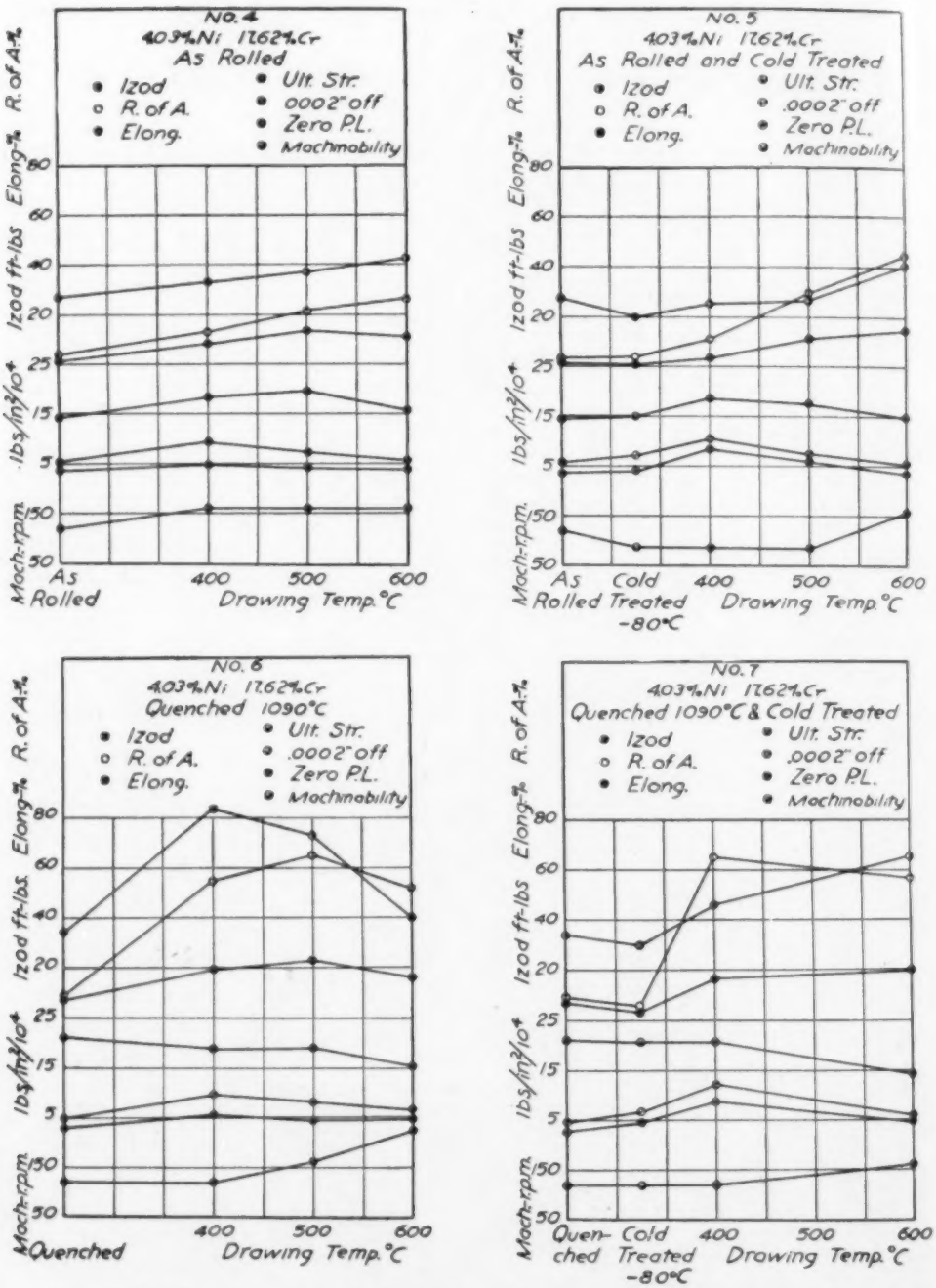


Fig. 3—Physical Properties of Steel Containing 17.62 Per Cent Chromium and 4.03 Per Cent Nickel. Chart No. 4, as Rolled. Chart No. 5, as Rolled Followed by Cold Treating. Chart No. 6, Brine-Quenched from 1090 Degrees Cent. Chart No. 7, Brine-Quenched from 1090 Degrees Cent. and Cold-Treated. Plotted from Data Shown in Table II.

on the threaded end of the tensile specimens. The bars used for determining magnetic permeability measured ½ inch square and

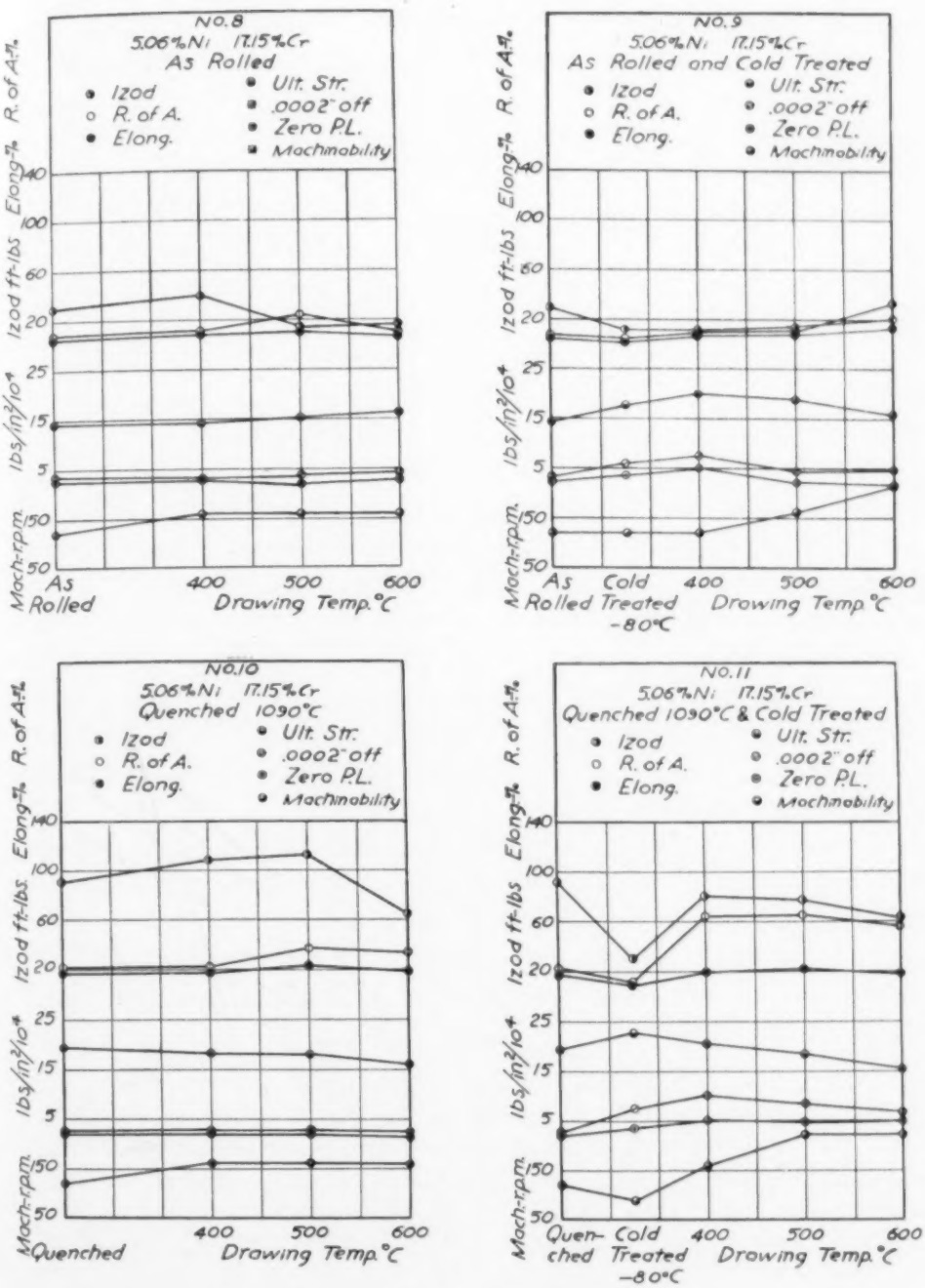


Fig. 4—Physical Properties of Steel Containing 17.15 Per Cent Chromium and 5.06 Per Cent Nickel. Chart No. 8, as Rolled. Chart No. 9, as Rolled, Followed by Cold Treating. Chart No. 10, Brine-Quenched from 1090 Degrees Cent. Chart No. 11, Brine-Quenched from 1090 Degrees Cent. and Cold-Treated. Plotted from Data shown in Table III.

were tested at a magnetizing force of 300 Gilberts per centimeter. Specimens for specific volume were one centimeter square and 2.7

centimeters long, weighing approximately 22 grams. Determinations were made in the usual manner. Specimens were ground and finished on 00-French emery all over, and were then cleaned with petroleum ether. Weights were obtained in air and water, using brass weights on a Troemner analytical balance having a sensitivity of 0.1 milligram with a 200 gram load. Corrections were made for loss of weight of the wires used for suspension. Wires so weighed were always submerged to the same depth. All tests were made with distilled water and steel at a temperature of 20 degrees Cent.

Figs. 3 and 4 show graphically the tensile, Izod and machinability values given in Tables II and III, while Fig. 5 shows Brinell hardness, permeability and specific volume results.

In general the results indicate clearly that the 4.03 per cent nickel alloy is only slightly responsive to cold treatment, due presumably to the fact that the preliminary treatments leave it largely in the martensitic condition. The 5.06 per cent nickel alloy, however, shows a marked change in physical properties upon cold treatment, in the direction indicating austenitic transformation. The lower graphs in Fig. 5 are quite interesting in this respect, showing the surprising increase in Brinell hardness from 277 up to a maximum of 444, with a corresponding marked increase in volume and magnetic permeability.

Attention is called particularly to the comparison in behavior between specimens which were cold-treated before the draw, and those which were not cold-treated, but given the drawing treatment only. The latter show no increase whatever in hardness, and, as would be expected, no increase in permeability nor volume, remaining practically austenitic.

Table IV

Tensile Tests at Elevated Temperatures For Steel No. 6

Containing 17.15% Cr—5.06% Ni—Brine Quenched from 1090° C., Cold Treated —80° C. (—112° F.) and Drawn at 500° C. (930° F.)

Treatment	Proportional Limit Lbs./sq. in.	Ultimate Tensile Lbs./sq. in.	Elong. in 2" %	Reduction of Area %
Tested at 200° C.	115,000	147,300	18.6	64.5
Tested at 300° C.	115,000	142,500	17.0	62.6
Tested at 400° C.	95,000	132,000	16.0	63.5
Tested at 500° C.	65,000	117,500	16.2	63.3
No cold treatment before drawing at 500° C.				
Tested at 200° C.	65,000	137,200	19.6	65.2
Tested at 300° C.	65,000	118,400	24.8	65.2
Tested at 400° C.	55,000	117,100	21.5	63.5
Tested at 500° C.	60,000	104,500	19.7	69.7

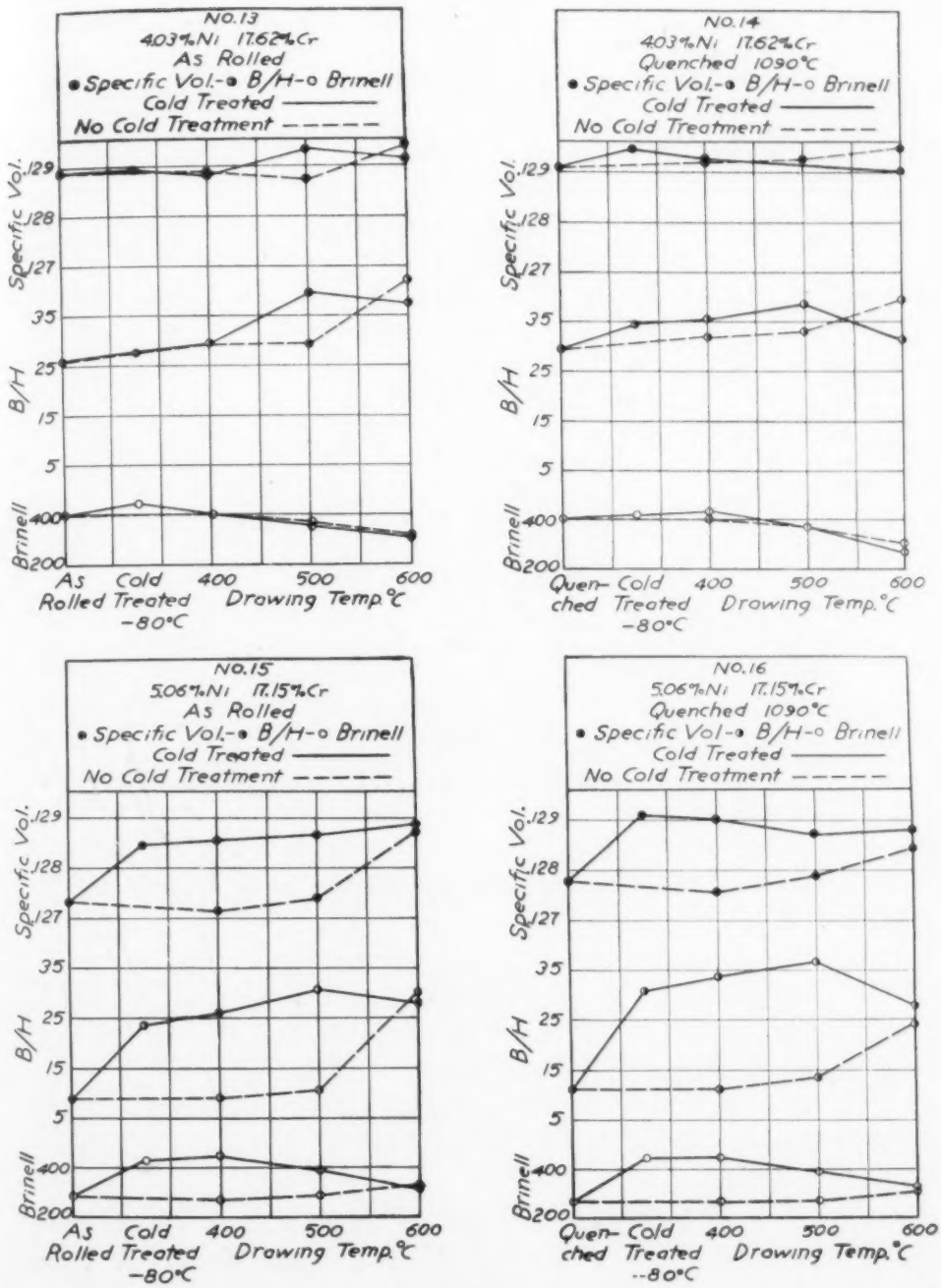


Fig. 5—Specific Volume, Brinell Hardness and Permeability of Steels Nos. 5 and 6 after Various Treatments. Chart No. 13, 17.62 Per Cent Chromium, 4.03 Per Cent Nickel Steel No. 5 As-rolled and Drawn, Compared with same Steel Cold-treated and Drawn. Chart No. 14, Steel No. 5 Quenched at 1090 Degrees Cent. and Drawn. Compared with Same Steel Quenched, Cold-treated and Drawn. Charts Nos. 15 and 16. Same as Nos. 13 and 14 for Steel No. 6 Containing 17.15 Per Cent Chromium and 5.06 Per Cent Nickel. Note Great Increase in Charts Nos. 15 and 16 of Hardness and Permeability in Steels which were Cold-treated Before the Draw as Compared to those which were not Cold-treated.

Of practical interest are the excellent physical properties shown in Table III for the bar quenched, cold-treated and drawn, suggesting the use of this analysis in springs or shock resisting parts. The Izod values of 77 and 81 foot-pounds obtained on this treatment

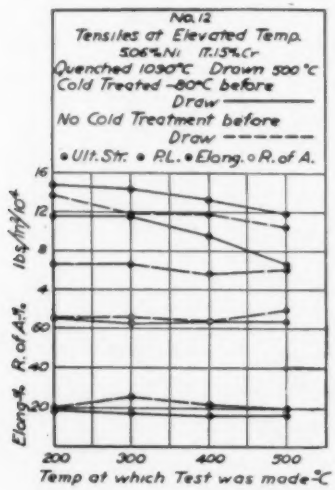


Fig. 6—Tensile Tests at Elevated Temperatures on Steel No. 6 Containing 5.06 Per Cent Nickel After Various Treatments. Plotted from Data Given in Table IV.

are particularly noteworthy. The improvement noted in machining characteristics after the treatment appears to have interesting possibilities.

In order to obtain some general information on the adaptability of the 18.00 per cent chromium 5.00 per cent nickel analysis to high temperature work, a few tensile tests were made at elevated temperatures upon specimens brine-quenched, cold-treated to —80 degrees Cent. (—112 degrees Fahr.) and drawn at 500 degrees Cent. (930 degrees Fahr.). These are shown in detail in Table IV, and graphically in Fig. 6.

Figs. 7 to 11 inclusive show typical microstructures corresponding to the various treatments for the two steels shown in Tables II and III.

All the specimens were etched in aqua regia and glycerine. The aqua regia was composed of three parts concentrated hydrochloric acid and one part concentrated nitric acid. Forty parts of this solution were used for sixty parts of glycerine. Micrograph A of Fig. 7 shows a structure characteristic of the 5.06 per cent nickel-17.15

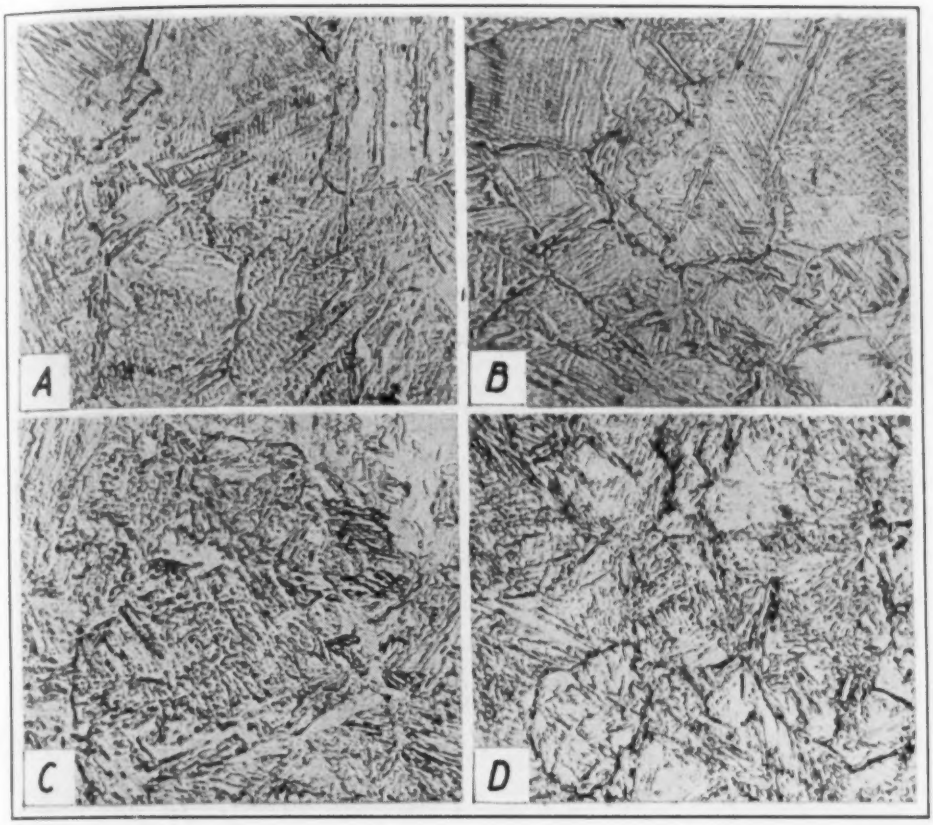


Fig. 7—Steel Containing 5.06 Per Cent Nickel, 17.15 Per Cent Chromium. A—As-rolled; B—As-rolled and Cold-treated —80 Degrees Cent.; C—As-rolled Cold-treated —80 Degrees Cent., Drawn at 400 Degrees Cent.; D—As-rolled, Cold-treated —80 Degrees Cent., Drawn at 500 Degrees Cent. All Micrographs × 1000—Etched in Aqua Regia and Glycerine.

per cent chromium alloy in the rolled condition. The second-order grains are usually quite well-defined and contain distinctive cleavage plane configurations. B of Fig. 7 shows little change after cold treating with the exception of fine acicular markings in many of the grains. In C and D the martensitic markings nearly cover the entire area within the grains. In Fig. 8, micrograph A, the martensite is completely broken to ferrite and a dark sorbitic-like constituent. If micrograph B, Fig. 8, of the rolled specimen drawn at 400 degrees Cent. (750 degrees Fahr.) without the cold treatment be compared to micrograph C, Fig. 7, the effect of cold treatment followed by drawing will be evident. In C, Fig. 7, the martensite is rather well developed, while B, Fig. 8, is not unlike A, Fig. 7, which is in the as-rolled condition. A like comparison may be drawn between C, Fig. 8, and D, Fig. 7. Micrograph D, Fig. 8, which was drawn at

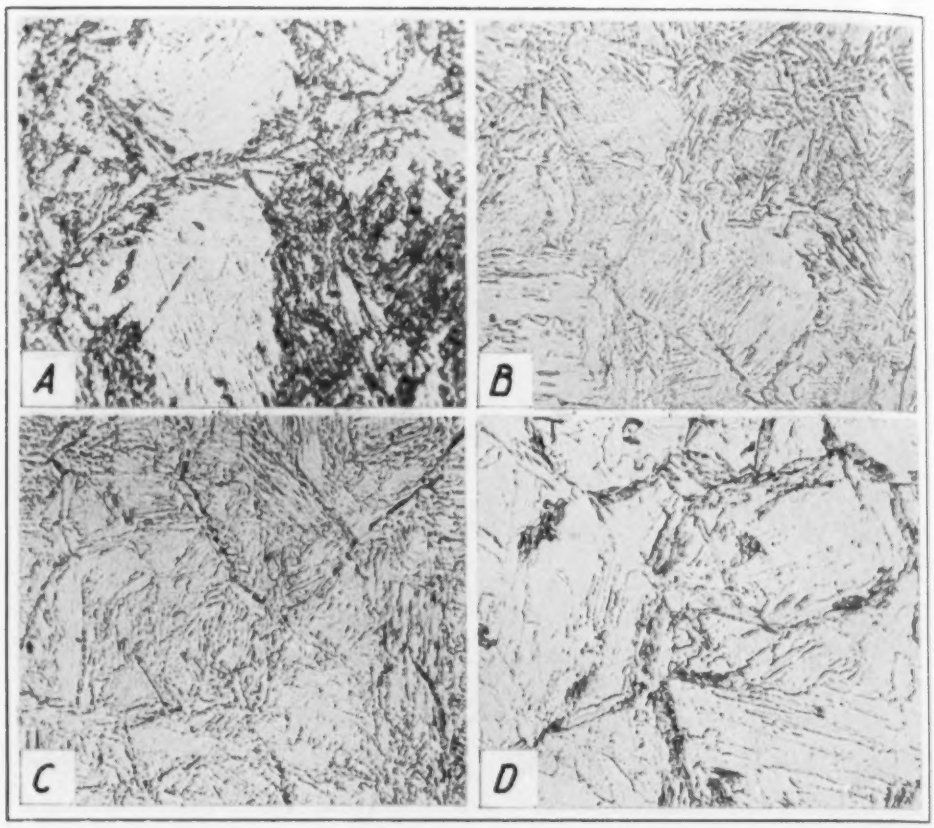


Fig. 8—Steel Containing 5.06 Per Cent Nickel, 17.15 Per Cent Chromium. A—As-rolled, Cold-treated —80 Degrees Cent., Drawn 600 Degrees Cent.; B—As-rolled, Drawn at 400 Degrees Cent.; C—As-rolled, Drawn at 500 Degrees Cent.; D—As-rolled, Drawn at 600 Degrees Cent. All Micrographs × 1000—Etched in Aqua Regia and Glycerine.

600 degrees Cent. (1110 degrees Fahr.) without cold treatment shows only a small amount of the sorbitic constituent which composed at least 75 per cent of A, Fig. 8, which was cold-treated before drawing at 600 degrees Cent. (1110 degrees Fahr.). These sorbitic nodules probably represent the total amount of martensite present in the specimens as rolled, which has now been broken down in drawing. Micrograph A, Fig. 9, shows the structure peculiar to the 5.06 per cent nickel-17.15 per cent chromium alloy after brine quenching from 1090 degrees Cent. (1995 degrees Fahr.). The grain boundaries are less distinct than in the rolled specimens and the cleavage planes more pronounced. Micrographs B, C and D, Fig. 9, show the martensitic development and general darkening of the fields as the drawing temperature increases. Micrograph A, Fig. 10, after water quenching at 1090 degrees Cent., (1995 degrees Fahr.) cold treating at —80 degrees Cent., (—112 degrees Fahr.) and drawing

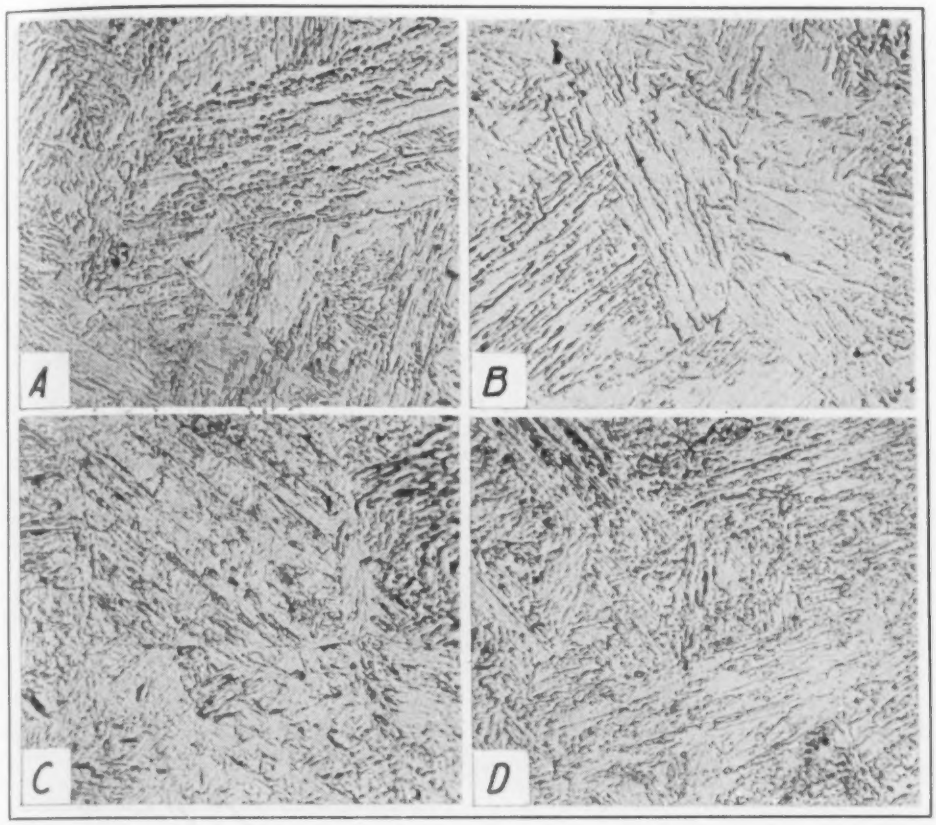


Fig. 9—Steel Containing 5.06 Per Cent Nickel, 17.15 Per Cent Chromium. A—Water-quenched from 1090 Degrees Cent.; B—Water-quenched from 1090 Degrees Cent., Cold-treated —80 Degrees Cent.; C—Water-quenched from 1090 Degrees Cent., Cold-treated —80 Degrees Cent., Drawn at 400 Degrees Cent.; D—Water-quenched from 1090 Degrees Cent., Cold-treated —80 Degrees Cent., Drawn at 500 Degrees Cent. All Micrographs × 1000. Etched in Aqua Regia and Glycerine.

at 600 degrees Cent. (1110 degrees Fahr.) shows the formation of the sorbitic constituent as in A, Fig. 8, except that the ferrite patches are entirely absent here. Specimens quenched at 1090 degrees Cent. (1995 degrees Fahr.) and drawn at 400, 500 and 600 degrees Cent. (750, 930, 1110 degrees Fahr.) without cold treatment represented by micrographs B, C and D, Fig. 10, show very little change in structure when compared to quenched specimen A, Fig. 9. It is interesting to note, however, that no sorbite was produced in D, Fig. 10, which was quenched and drawn at 600 degrees Cent. (1110 degrees Fahr.) with no cold treatment. This supports the view that in the rolled condition there was a small amount of martensite developed due to the atomic agitation produced by low finishing temperature on the mill. This martensite later broke down to sorbite during drawing as shown in D, Fig. 8. The entire absence of sorbite in D,

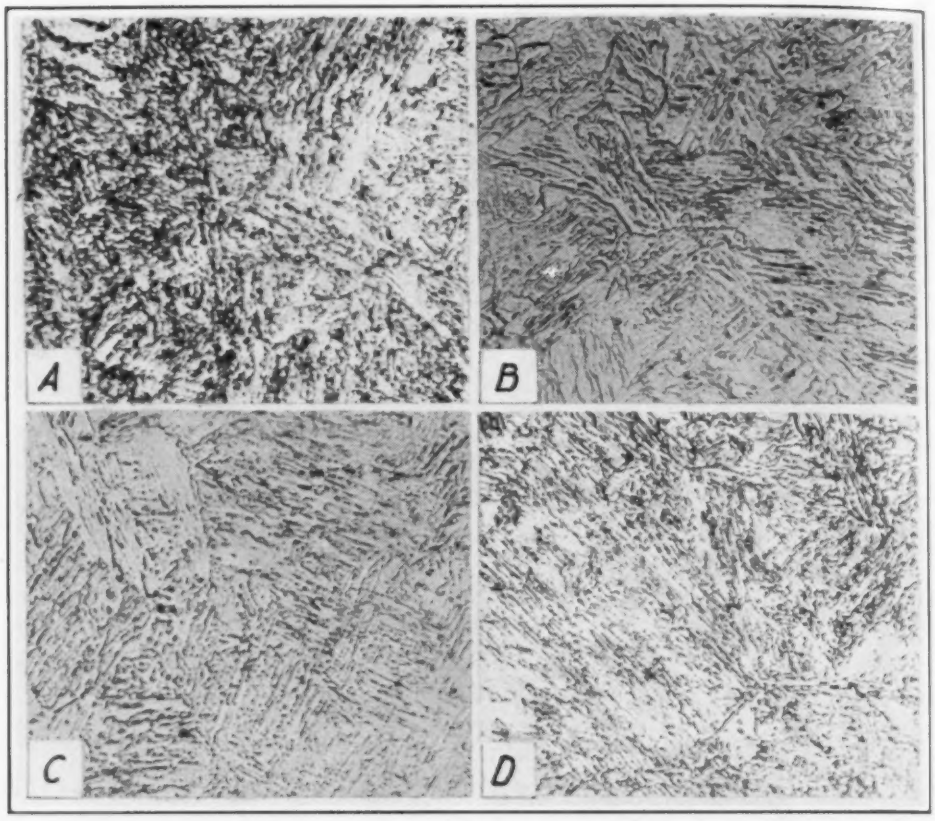


Fig. 10—Steel Containing 5.06 Per Cent Nickel, 17.15 Per Cent Chromium. A—Water-quenched 1090 Degrees Cent., Cold-treated —80 Degrees Cent., Drawn 600 Degrees Cent.; B—Water-quenched 1090 Degrees Cent.; Drawn 400 Degrees Cent.; C—Water-quenched 1090 Degrees Cent., Drawn 500 Degrees Cent.; D—Water-quenched 1090 Degrees Cent., Drawn 600 Degrees Cent. All Micrographs × 1000. Etched in Aqua Regia and Glycerine.

Fig. 10, undoubtedly shows that the alloy was fully austenitic after quenching at 1090 degrees Cent. (1995 degrees Fahr.). All of the martensite that was present due to cold finishing had been entirely converted to austenite and retained as such by the quenching. It naturally follows that without cold treating, no martensite was produced that might subsequently be broken down to sorbite when drawn. However the existence of an A_2 at approximately 600 degrees Cent. (1110 degrees Fahr.) whether or not the steel was cold treated will be discussed later.

The micrographs of the 4.03 per cent nickel-17.62 per cent chromium alloy given in A and B of Fig. 11 show the presence of ferrite in both the rolled and quenched condition. Cold treating has little effect on this alloy since its critical points are sufficiently above room temperature for it to be in the martensitic condition as rolled.

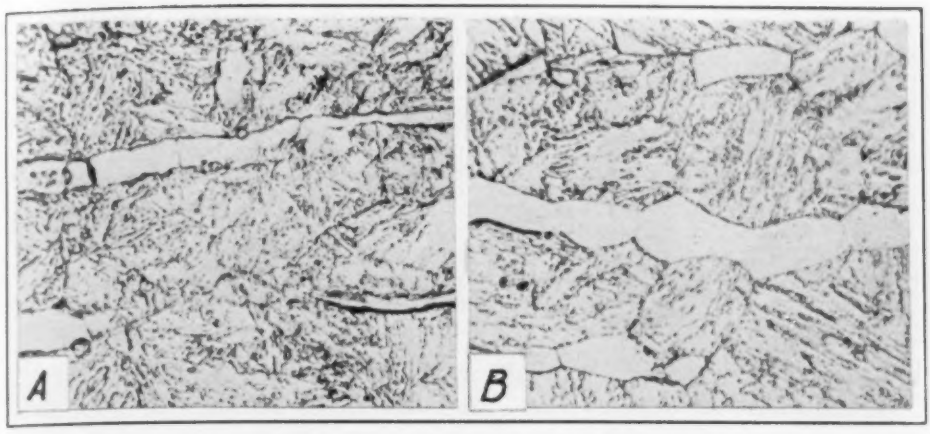


Fig. 11—Steel Containing 4.03 Per Cent Nickel, 17.62 Per Cent Chromium. A—Water-quenched 1090 Degrees Cent., Cold-treated —80 Degrees Cent., Drawn at 600 Degrees Cent.; B—As-rolled, Cold-treated —80 Degrees Cent., Drawn 600 Degrees Cent. All Micrographs × 1000. Etched in Aqua Regia and Glycerine.

Quenching likewise does not suppress the transformation to such an extent that martensite is not present at room temperature.

It is interesting to note in passing that the presence of 0.08 to 0.10 per cent carbon is necessary in 5.00 per cent nickel alloys to prevent the formation of ferrite. For instance, an alloy analyzing 5.09 per cent nickel-17.35 per cent chromium with only 0.05 per cent carbon contained considerable amounts of ferrite as rolled. However it is materially decreased by brine quenching from 1090 degrees Cent. (1995 degrees Fahr.). This low carbon alloy had a hardness of 340 Brinell as rolled and 332 Brinell as quenched from 1090 degrees Cent. (1995 degrees Fahr.). Nevertheless, it was found to be susceptible to cold treatment. A quenched specimen showed a Brinell of 401 after cold treating at —80 degrees Cent., (—112 degrees Fahr.) and drawing at 100 degrees Cent. From the high hardness obtained as forged and as quenched, it is possible that small variations in carbon exert an important influence on the position of the wholly austenitic field and the mixed structure field composed of martensite and austenite.

Salt spray tests were made upon specimens in the various conditions shown in Tables II and III. The specimens measured ¾ inch in diameter with a cone having an apex angle of sixty degrees. Specimens were finished first with a file, and then with Three Mite 120, followed by 150 grain emery cloth, and were exposed to a 5 per cent salt spray for 120 hours. Results are shown in Figs. 12 and 13.

In general the 5.06 per cent nickel steel is more resistant to salt

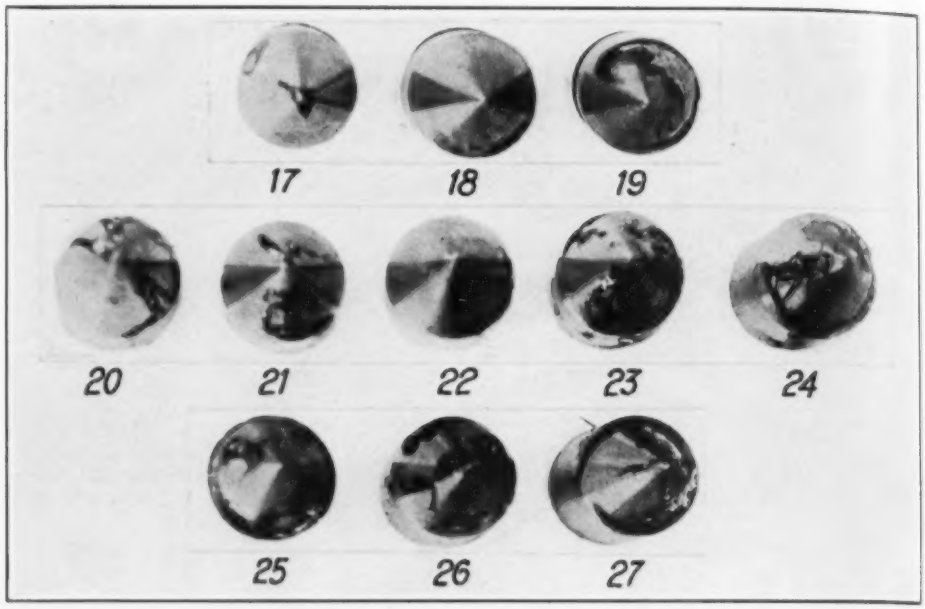


Fig. 12—Salt Spray Tests on Steel No. 15 Containing 4.03 Per Cent Nickel. Five Per Cent Salt Spray 100 Hours. Physical Properties Corresponding to These Tests are Shown in Table II.

17—Quenched at 1090° C., no cold treatment, drawn at 400° C.
18—Quenched at 1090° C., no cold treatment, drawn at 500° C.
19—Quenched at 1090° C., no cold treatment, drawn at 600° C.
20—As-rolled.
21—As-rolled and cold-treated at —80° C.
22—As-rolled and cold-treated at —80° C., drawn at 400° C.
23—As-rolled and cold-treated at —80° C., drawn at 500° C.
24—As-rolled and cold-treated at —80° C., drawn at 600° C.
25—As-rolled, no cold-treatment, drawn at 400° C.
26—As-rolled, no cold-treatment, drawn at 500° C.
27—As-rolled, no cold-treatment, drawn at 600° C.

spray corrosion than the lower nickel. With the 5.06 per cent nickel it is noteworthy that while in the pieces quenched before the cold treatment, corrosion does not start until a drawing temperature of 600 degrees Cent. is reached, in those cold-treated without the preliminary treatment it is not safe to draw over approximately 400 degrees Cent. (750 degrees Fahr.). This seems to indicate an increase in corrosion resistance resulting from the preliminary quench. Later tests made for 100 hours in 20 per cent salt spray checked the results obtained in 5 per cent salt spray.

The work thus far had demonstrated the possibility of improving the physical properties of the chromium-nickel alloys by cold treatment, indicating an optimum at approximately 5 per cent nickel. However a few experiments with steels slightly higher than 5 per cent indicated that the nickel limits for best results when cooling to —80 degrees Cent. (—112 degrees Fahr.) in dry ice, were rather

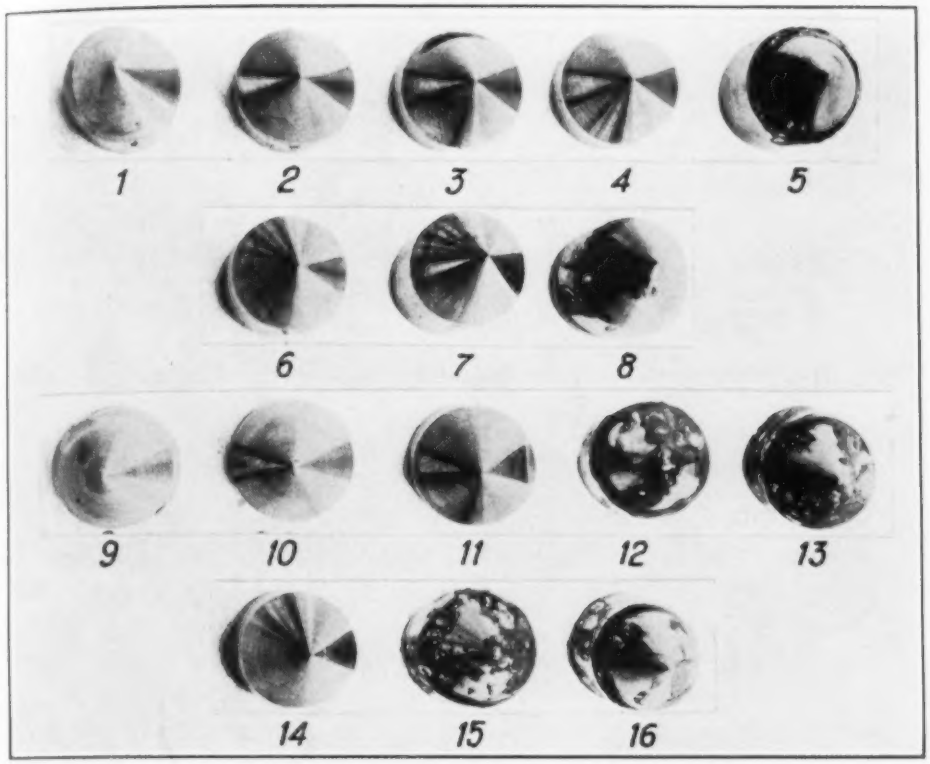


Fig. 13—Salt Spray Tests on Steel No. 6, Containing 5.06 Per Cent Nickel. Five Per Cent Salt Spray 100 Hours. Physical Properties Corresponding to These Tests are Shown in Table III.

1—Quenched at 1090° C.
2—Quenched at 1090° C., cold-treated —80° C.
3—Quenched at 1090° C., cold-treated —80° C., drawn at 400° C.
4—Quenched at 1090° C., cold-treated —80° C., drawn at 500° C.
5—Quenched at 1090° C., cold-treated —80° C., drawn at 600° C.
6—Quenched at 1090° C., no cold-treatment, drawn at 400° C.
7—Quenched at 1090° C., no cold-treatment, drawn at 500° C.
8—Quenched at 1090° C., no cold-treatment, drawn at 600° C.
9—As-rolled.
10—As-rolled, cold-treated —80° C.
11—As-rolled, cold-treated —80° C., drawn 400° C.
12—As-rolled, cold-treated —80° C., drawn 500° C.
13—As-rolled, cold-treated —80° C., drawn 600° C.
14—As-rolled, no cold-treatment, drawn at 400° C.
15—As-rolled, no cold-treatment, drawn at 500° C.
16—As-rolled, no cold-treatment, drawn at 600° C.

narrow. It therefore seemed desirable to accurately determine the maximum nickel content allowable. Since all the cooling treatments up to this time had been conducted without attention to cooling rate, it also appeared desirable to determine the A_r and A_c points, and to study the influence of cooling rate upon their location. Consequently further work was laid out to investigate the following points:

a—Influence of small variations of nickel upon response to cold treatment.

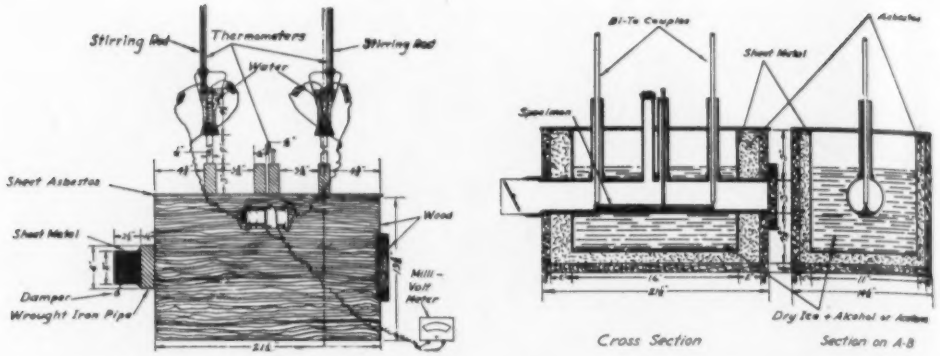


Fig. 14—Assembly and Section of Cold Muffle Showing Thermocouples in Place.

b—Location of A_r and A_c points.

c—Influence of rate of cooling upon location of the A_r point.

d—Effect of element of time upon results of treatment.

e—Effects of lower temperatures than —80 degrees Cent. (—112 degrees Fahr.) as commercially attainable with dry ice.

In order to obtain the controlled cooling and accurate temperature measurement essential to the study of these factors, it was necessary to devise, first, a container capable of maintaining low tem-

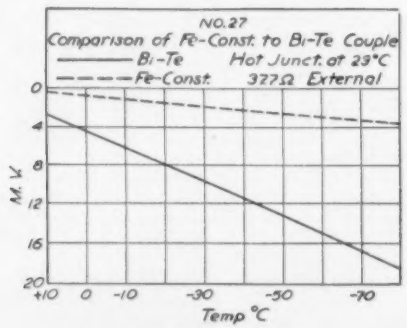


Fig. 15—Characteristics of Bismuth-tellurium Couple as Compared to Iron-constantan Through the Range of 10 to —80 Degrees Cent.

peratures within close limits, and second, a thermocouple of greater accuracy at the low temperatures than those commonly available. The container took the form of a low temperature muffle as shown in Fig. 14.

The construction of this muffle was extremely simple. It merely consisted of a wooden box approximately 14 x 14 x 21 inches, with holes cut in the ends to allow the insertion of a 3-inch wrought iron pipe. A rectangular tank, 11 x 11 x 16 inches of galvanized sheet

iron was placed in the box and surrounded on all sides and the bottom with a 2-inch layer of tightly packed asbestos fiber. The wrought iron pipe after insertion was soldered to the tank. The pipe had been previously drilled on one side and 1-inch nipples welded over the holes. Short lengths of pipe were then screwed in the nipples for thermocouple wells. A sliding wooden door was made at one end of the muffle. The other end contained a damper. With this

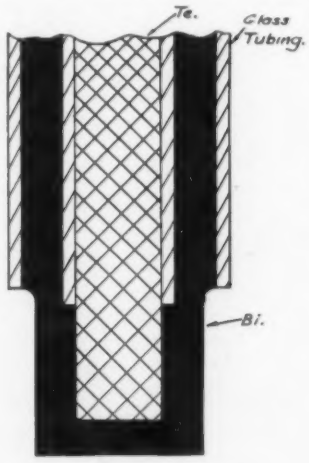


Fig. 16

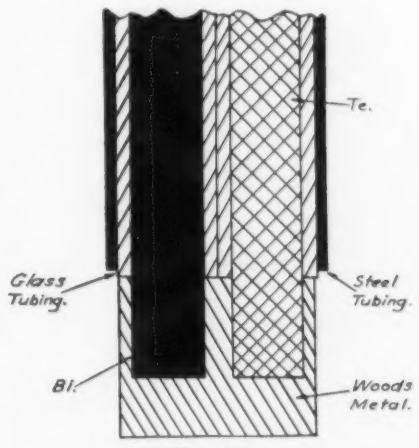


Fig. 17

Fig. 16—Detail of Cold Junction Construction of Bismuth-tellurium Couple Using One Annular Element and One Cylindrical Element.
Fig. 17—Detail of Cold Junction Construction of Bismuth-tellurium Couple Using Two Cylindrical Elements.

system of ventilation, it was possible to keep the temperature to ± 1 degree Cent. throughout the whole temperature range of + 10 to —80 degrees Cent. over periods as long as eight hours. When the apparatus was in use alcohol and acetone were added in sufficient amounts to completely cover the muffle. Solid CO_2 in small lumps was added gradually until the required temperature was reached. Even at very low temperatures the evolution of gas kept the liquor in constant motion which insured a uniform temperature. During operation the top of the container was covered with a ¼ inch thick asbestos board which could be raised from time to time to allow the additions of solid CO_2. The apparatus as shown in Fig. 14 is arranged for the treatment of bars for the interrupted magnetic test.

Turning now to the accurate measurement of sub-zero temperatures, this was a troublesome problem in the early stages of the work. The ordinary iron-constantan couple can be used by reversing the leads and calibrating the millivoltmeter. However this couple only generates 0.031 millivolts per degree centigrade between +10 and

—80 degrees Cent. Obviously it could not be used except for rough estimates of temperature and could not be considered at all when attempts were made to determine the A_r points. Some use was made of toluene thermometers from +50 to —100 degrees Cent. (—148 degrees Fahr.) and pentane thermometers for temperatures from +50 to —200 degrees Cent. (—328 degrees Fahr.). The use of

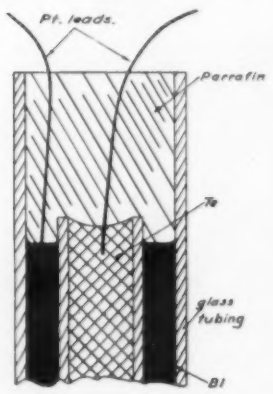


Fig. 18

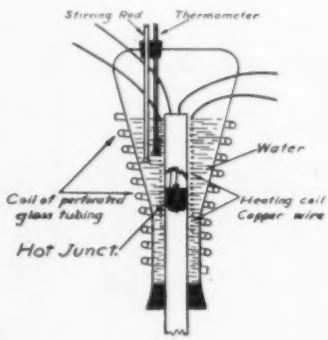


Fig. 19

Fig. 20

Fig. 18—Detail of Hot Junction, Bismuth-tellurium Couple.
Fig. 19—Details of Constant Temperature Cell for Hot Junction of Bismuth-tellurium Couple.
Fig. 20—Assembly of Bismuth-tellurium Thermocouple.

thermometers however was restricted since they were too sluggish to record small fluctuations in temperature and could not be used for the determination of critical points.

The most satisfactory instrument for the measurement of temperatures from +20 to —180 degrees Cent. (—292 degrees Fahr.) is the bismuth-tellurium couple. The characteristics of this couple and other combinations with tellurium have been previously determined by Lewitsky and Lukomsky[9] and Lange and Heller[10]. A comparison of the bismuth-tellurium couple with the iron-constantan couple is given in Fig. 15. With the hot junction at 23 degrees Cent., an 18-inch couple generated 0.180 millivolts per degree centigrade, thus generating about six times the electromotive force as the iron-constantan couple.

Two methods were employed in making couples. In one a glass

[9]M. A. Lewitsky and M. A. Lukomsky, "Das Thermoelement Te/Bi und seine praktischen Anwendungen," *Physikalische Zeitschrift*, Vol. XXX, 1929, p. 203.

[10]B. Lange and W. Heller, "Tellur-Thermoelemente," *Physikalische Zeitschrift*, Vol. XXX, 1929, p. 419.

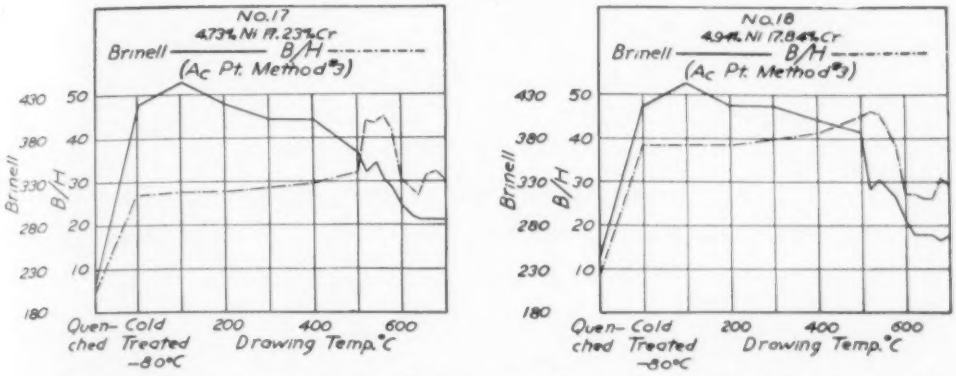


Fig. 21, Chart No. 17—Brinell Hardness and Permeability of 4.73 Per Cent Nickel Alloy (Steel No. 7) After Successive Treatments Shown.
Chart No. 18—Brinell Hardness and Permeability of 4.94 Per Cent Nickel Alloy (Steel No. 8) After Successive Treatments Shown.

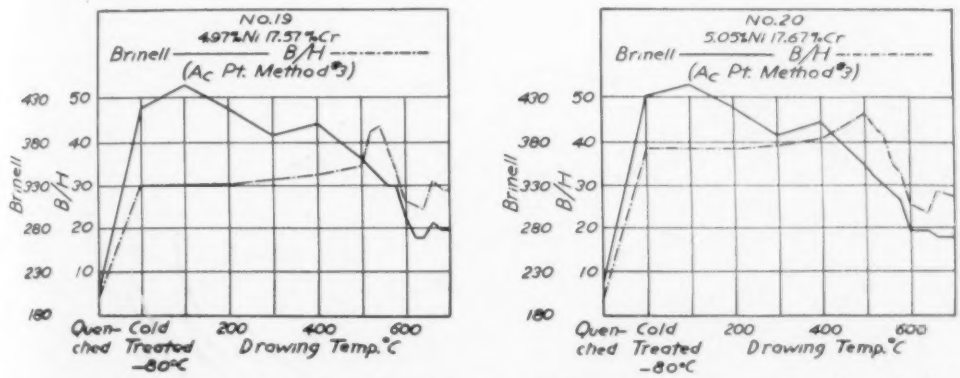


Fig. 22, Chart No. 19—Brinell Hardness and Permeability of 4.97 Per Cent Nickel Alloy (Steel No. 9) After Successive Treatments Shown.
Chart No. 20—Brinell Hardness and Permeability of 5.05 Per Cent Nickel Alloy (Steel No. 10) After Successive Treatments Shown.

tube with a $\frac{3}{16}$ inch bore was cast full of tellurium. This is an extremely difficult procedure. Various methods were tried, such as drawing molten tellurium through a hot tube with a vacuum pump. However the tellurium element invariably cracked in several places on cooling. The most successful method was as follows: Tellurium was ground to pass a 100 mesh sieve, and a well annealed glass tube was filled with the powder. The low flame of a Bunsen burner was applied to the tube until the tellurium became molten. During the heating operation the tube was rotated and shaken gently. Gradually an element of tellurium of sufficient length was produced. The glass at one end of the element was cracked off by heating and plunging into water. The tellurium element was then placed in a ½ inch glass tube and bismuth ground to pass a 75 mesh sieve was packed around the element. The bismuth element was melted in the same

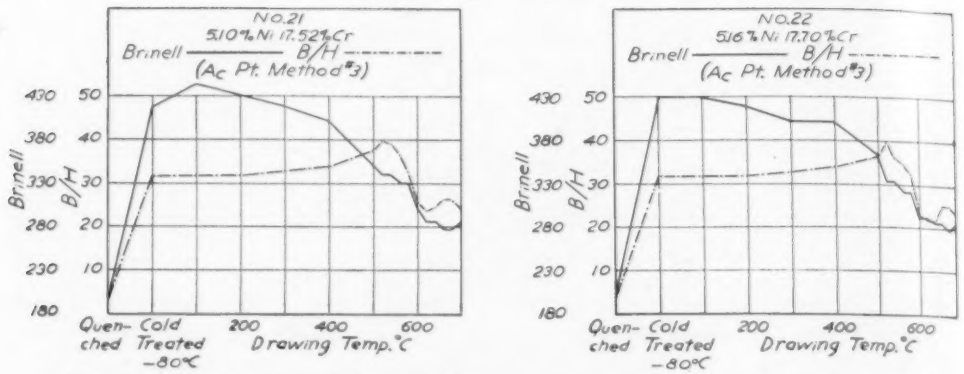


Fig. 23, Chart No. 21—Brinell Hardness and Permeability of 5.10 Per Cent Nickel Alloy (Steel No. 11) After Successive Treatments Shown.
Chart No. 22—Brinell Hardness and Permeability of 5.16 Per Cent Nickel Alloy (Steel No. 12) After Successive Treatments Shown.

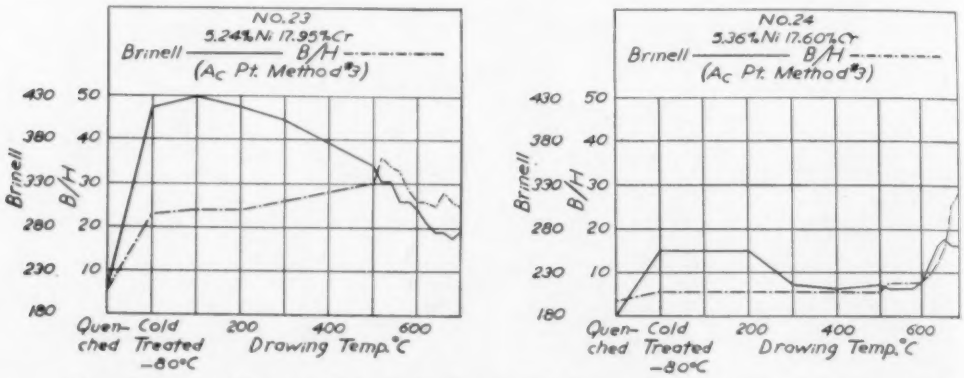


Fig. 24, Chart No. 23—Brinell Hardness and Permeability of 5.24 Per Cent Nickel Alloy (Steel No. 13) After Successive Treatments Shown.
Chart No. 24—Brinell Hardness and Permeability of 5.36 Per Cent Nickel Alloy (Steel No. 14) After Successive Treatments Shown.

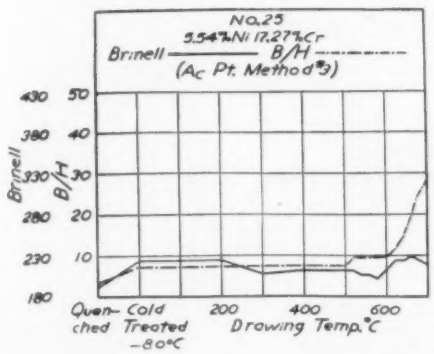
fashion as the tellurium. The glass at the end of the bismuth was cracked off by heating and plunging into water. The cold junction construction of a couple of this type is shown in Fig. 16.

Couples were also made of separate elements of bismuth and tellurium and placed in steel tubes. The glass from one end of the elements was removed in the manner given above. The exposed ends were placed in a split steel mold and Wood's metal cast around them. The cold junction of such a couple is shown in Fig. 17. The steel tube may be filled with paraffine or sealing wax to keep the elements in position. This type of couple is considerably less fragile than the first described.

Hot junctions were made as shown in Fig. 18. Platinum leads were welded to the elements and incased in paraffine or sealing wax.

The temperature control of the hot junction is extremely im-

portant, since a rise of hot junction temperature of 1 degree Cent. will increase the reading 0.2 millivolts. However this characteristic is valuable when the magnification of readings is desired in a certain temperature range. The hot junction temperatures were controlled by means of a constant temperature cell shown in Fig. 19. This cell was made from an inverted 250 c. c. Erlenmeyer flask with holes cut in bottom and sides for thermometer, stirring rod



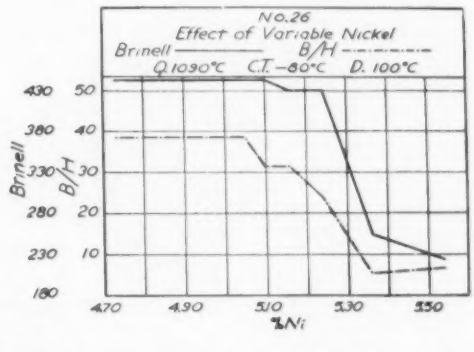


Fig. 25 Chart No. 25—Brinell Hardness and Permeability of 5.54 Per Cent Nickel Alloy (Steel No. 15) After Successive Treatments Shown.

Fig. 26—Maximum Hardness, and Corresponding Permeability, of Series of Steels of Different Nickel Content. Brine Quenched 1090 Degrees Cent., Cold-treated —80 Degrees Cent., Drawn at 100 Degrees Cent. Permeability Determined for H = 200. Compiled from Figs. 21 to 25 Inclusive.

and element wires. The cell may be filled with water or oil. The elements were so arranged that the hot junction was well submerged in the bath. Heating was accomplished by a copper coil attached to a storage battery. The whole cell was wrapped in cotton. If gradual cooling was desired the cotton was wet with ether and natural evaporation allowed to take place. When rapid cooling was desired, the cotton was wet with ether, and air was blown through the perforated glass coil shown on the outside of the cell in Fig. 19. The bath was constantly kept in motion by means of a stirring rod. Complete assembly of the thermocouples is shown in Figs. 14 and 20.

With the aid of the low temperature muffle and the bismuth-tellurium couple it was possible not only to regulate heating and cooling rates, but also to detect very slight thermal effects, so that this apparatus lent itself admirably to the study of the five factors already mentioned. These will now be discussed.

a—*Influence of Small Variations of Nickel upon Response to Cold Treatment:* A series of nine steels containing approximately 17.50 per cent chromium and ranging from 4.73 to 5.54 per cent nickel were made in 2-inch square ingots and forged to test bars

measuring 1 x ¼ inch. Complete analyses are shown in Table I, Steels 7 to 15 inclusive.

The bars were first quenched in brine from a temperature of 1090 degrees Cent., (1995 degrees Fahr.) after which they were Brinelled and then tested for permeability on a Fahy permeameter using a magnetizing force of 200 Gilberts per centimeter. They were then given the following successive treatments, allowed to return to room temperature after each treatment and tested for Brinell hardness and permeability: cold-treated at —80 degrees Cent., (—112 degrees Fahr.) cooling 2 degrees Cent. per minute; heated to tem-

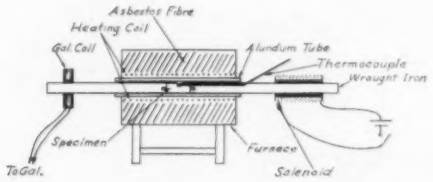


Fig. 27—Section of Apparatus Used in Determination of Magnetic Points by Method No. 2.

peratures from 100 to 700 degrees Cent. in steps of 100 degrees Cent., cooling in air in each case. Complete results upon the individual steels are shown graphically in Figs. 21 to 25 inclusive. The effect of nickel content upon maximum hardness attained is shown in Fig. 26, in which the average permeability corresponding to the maximum hardness reading is also indicated.

Attention is drawn to two features in connection with the results shown in Figs. 21 to 25 inclusive. First, the maximum Brinell hardness is obtained in every case with a drawing temperature of 100 degrees Cent. It is possible that this temperature corresponds to the final break-down of retained austenite, but if this is the case it is surprising that there is no corresponding increase in permeability. Comparing hardness curves in Figs. 21 to 25 inclusive with that shown for the 5.23 per cent nickel steel in Fig. 2, Chart No. 2, it will be seen that these curves differ considerably, secondary hardening in the 5.23 per cent nickel steel occurring at a higher temperature due probably to the faster cooling rate in cold treatment, with a consequent greater proportion of retained austenite.

Attention is next called to the peak in the permeability curve occurring at approximately 500 degrees Cent. (930 degrees Fahr.). This will be referred to later in the discussion of critical points.

Fig. 26 indicates that the maximum nickel content for effective

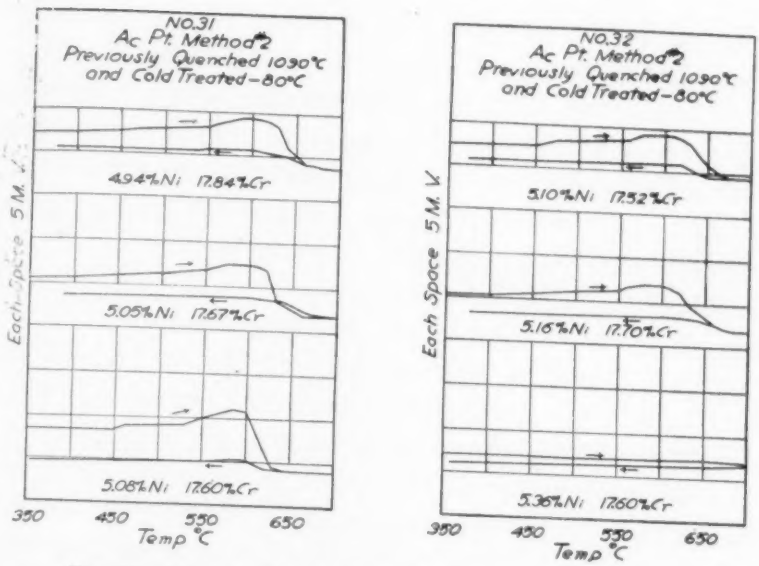


Fig. 28—Magnetic Points Determined by Method No. 2 Upon Six Alloys of Different Nickel Contents.

hardening by cold treatment occurs at 5.10 per cent and that alloys ranging from 4.70 per cent nickel to 5.10 per cent nickel might be expected to develop similar physical properties. It might be remarked that steel No. 6 containing 5.06 per cent nickel, upon which very complete test data are given earlier in the paper in Table III and accompanying diagrams, falls well within the optimum nickel range, so that the physical results shown in Table III may be considered as representative of the best practice known at the present time.

b—*Determination of A_r and A_c Points:* It was hoped that it would be possible to determine both the A_c and A_r points by thermal methods. However the only thermal point possible to detect was an A_r point found with the use of Bi-Te couples, which occurred below atmospheric temperature following a brine quench from 1090 degrees Cent. This point is probably A_r'', corresponding to the martensitic change in quenched carbon steel.

All the points determined above room temperature were determined by magnetic methods, two types of which were used. Since these points represent magnetic changes, to avoid pitfalls they should properly be referred to as Ac_2 and Ar_2. The three methods used in the determination of critical points will be referred to as methods 1, 2 and 3, and may be described as follows:

Method No. 1—This is the thermal method, and since the meth-

ods for determination of thermal points are well known, this need not be described in detail. The specimen used measured 1 inch in diameter x 1½ inches long, the bismuth-tellurium couple being imbedded in a ⅜ inch diameter axial hole. Specimens were cooled at predetermined rates in the low temperature muffle. In most cases time-temperature curves were plotted. When difference curves were desired, carbon steel was used as the neutral body.

Method No. 2—This is known as the continuous magnetic method, employing a modification of the magnetic apparatus described by Sauveur. This method is based on the fact that all steels unless they be austenitic, undergo a transformation on heating and lose their magnetism at a certain temperature known as the A_2 point. The magnetism is usually regained at a point slightly below this on cooling. The assembly of the apparatus is shown in Fig. 27. A wrought iron bar parted in the middle to include a specimen was placed in an electric resistance muffle. The specimens were 1 inch in diameter and 1 inch long, not including the threaded projection at each end. The wrought iron bar was also 1 inch in diameter and of sufficient length to extend at least a foot from each end of the muffle. Wrought iron was chosen since the A_c points of the alloys under discussion, as found by the interrupted method, were known to be below the A_2 point of iron. A solenoid composed of 200 turns of No. 18 D. C. C. copper wire wound on a fiber core connected through a key to a storage battery was used to magnetize the bar. Currents were induced in a secondary coil at the other end of the muffle composed of

Table V

Hardness of Specimens Used in Determination of Curve Shown in Fig. 32, by Interrupted Magnetic Method

5.08% Nickel—17.60% Chromium—Steel No. 16—Specimens at Temperature Four Hours Taken to Temperature Slowly and Cooled Back to Room Temperature Before Testing

Temperature Degrees Cent.	Temperature Degrees Fahr.	Brinell Hardness As Rolled	Brinell Hardness Quenched at 1090° C. (1995° F.)
+20	+68	285	269
+10	+50	285	269
+ 5	+41	293	269
0	+32	293	277
− 5	+23	341	363
−10	+14	388	388
−15	+ 5	388	388
−20	− 4	388	401
−30	−22	401	401
−40	−40	401	418
−50	−58	401	418
−60	−76	401	418
−70	−94	418	429
−80	−112	418	429

1500 turns of No. 27 S. C. C. copper wire. This coil was connected to a galvanometer so that quantitative data could be obtained. During operation these coils were kept at 25 degrees Cent. by means of an electric fan. Specimens were heated and cooled at the rate of 4 degrees a minute. When specimens entered the critical range, the

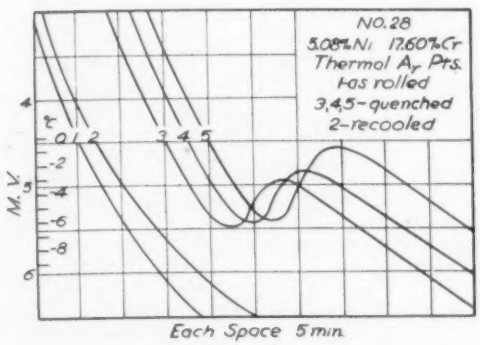


Fig. 29—Time-temperature Curves of 5.08 Per Cent Nickel (Steel No. 16). No. 1—As-rolled; No. 2—Specimen of Curve No. 3, Returned to Room Temperature and Recooled; No. 3—Quenched from 1090 Degrees Cent.; No. 4—Specimen from Curve No. 2, Quenched at 1090 Degrees Cent.; No. 5—Specimen Quenched at 1090 Degrees Cent.

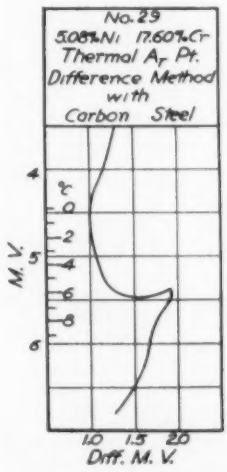


Fig. 30—Difference Curve Showing A_r'' Point on 5.08 Per Cent Nickel Steel. (Steel No. 16).

magnetic flux decreased. When the end of the range was reached, the magnetic flux ceased to pass. This action of course was reversed on cooling.

Method No. 3—This may be termed an interrupted magnetic method, and consists simply in determining the permeability of a standard magnet bar after various heatings and coolings. The method has already been referred to on page 504, and was used in obtaining the curves shown in Figs. 21 to 25 inclusive.

Fig. 28 gives the location of Ac_2 and Ar_2 points determined by Method No. 2 upon six steels of varying nickel content. Five of these steels are also included in Figs. 21 to 25 inclusive, showing the location of the Ac_2 point by the interrupted method. To the latter series has been added a steel containing 5.08 per cent nickel, the composition of which is shown in Table I as steel No. 16.

Comparison of Fig. 28 with Figs. 21 to 25 inclusive will be found interesting. Completion of the magnetic change on heating is shown on both sets of curves at about 650 degrees Cent. (1200 degrees Fahr.).

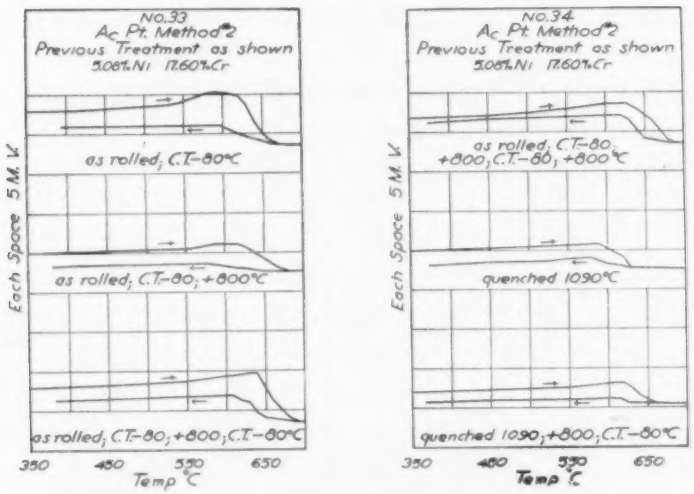


Fig. 31—Ar_2 and Ac_2 Points Upon 5.08 Per Cent Nickel Steel After Various Preliminary Treatments.

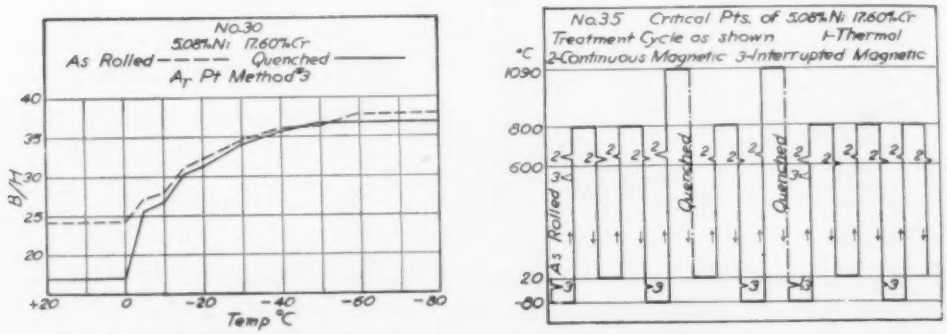


Fig. 32—Ar'' Point in 5.08 Per Cent Nickel Steel as Determined by Method No. 3.
Fig. 33—Composite Critical Points on Steel No. 16 Through Treatment Cycle Shown.

Since as already determined, a nickel content of 5.10 per cent appeared to be the optimum percentage for cold treatment, steel No. 16 containing 5.08 per cent nickel was selected for the further study of critical points. Using Method No. 1, time-temperature cooling curves were first made upon specimens both in the "as-rolled" and in the quenched conditions, several determinations being made to determine the reproducibility of the method. Fig. 29 shows a curve on the rolled material, and three curves on the quenched material. It will be seen from curves 3, 4 and 5, that checks within 1 degree Cent. are probably possible with this method. While no thermal point was found on the rolled specimen, a very marked point was found upon the quenched specimen at —6 degrees Cent., probably A_r'' as already suggested. Fig. 30 is a difference curve showing the same point, carbon steel having been used as the neutral body.

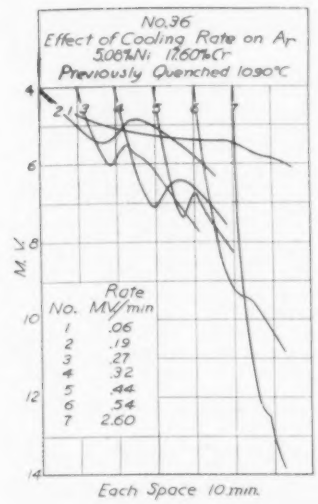


Fig. 34—Time-temperature Cooling Curves on Steel No. 16 Showing Effect of Cooling Rate Upon Position of Critical Point.

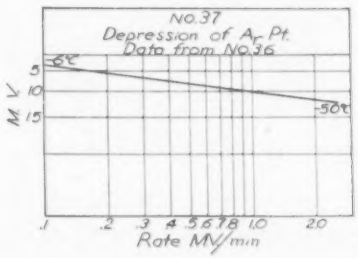


Fig. 35—Graph Showing Depression of Critical Point with Increase in Cooling Rate.

Ac_2 and Ar_2 points were determined, using Method No. 2, upon specimens which had been given the following preliminary treatments:

a—As rolled, cold-treated at —80 degrees Cent. (—112 degrees Fahr.).

b—As rolled, cold-treated at —80 degrees Cent., then heated to 800 degrees Cent. (1470 degrees Fahr.).

c—As rolled, cold-treated at —80 degrees Cent., heated to 800 degrees Cent., cold-treated at —80 degrees Cent.

d—As rolled, cold treated at —80 degrees Cent., heated to 800 degrees Cent., cold-treated at —80 degrees Cent., again heated to 800 degrees Cent.

e—Quenched at 1090 degrees Cent. in brine.

f—Quenched at 1090 degrees Cent. in brine, heated to 800 degrees Cent., and cold-treated at —80 degrees Cent.

Resulting curves are shown in Fig. 31. The A_r'' point was next determined by Method No. 3 upon both "as-rolled" and quenched specimens, as shown in Fig. 32.

Specimens were cooled slowly to temperature, and held four hours. Brinell hardness after various treatments is shown in Table V. It will be seen that a sharp increase in permeability occurs at

Table VI
Summary of Critical Points Upon Steels of Variable Nickel Content

No.	Ni	Cr	Ac_2 Interrupted Magnetic Method No. 3	Ac_2 Range Continuous Magnetic Method No. 2	Ar_2 Range Continuous Magnetic Method No. 2	Ar'' Range Interrupted Magnetic Method No. 3	Ar'' Thermal Method
7	4.73%	17.23%	530° C.	630/690° C.	680/620° C.	0/—60° C.	—6° C.
8	4.94	17.84	510	600/680	670/600	0/—60	—5
9	4.97	17.57	520	610/680	660/610	—5/—50	—7
10	5.05	17.67	500	610/680	660/600	—5/—60	—6.5
11	5.10	17.52	510	610/670	650/620	—5/—60	—7
12	5.16	17.70	510	600/680	670/620	—5/—70	—8
13	5.24	17.95	510	600/670	650/600	0/—60	—8?
14	5.36	17.60	None	None	None	None	None
15	5.54	17.27	None	None	None	None	None
16	5.08	17.60	510	600/680	660/600	0/—50	—6

—5 degrees Cent., checking closely the thermal curves upon the same steels shown in Figs. 29 and 30. However the range through which transformation is taking place probably extends from 0 to —60 degrees Cent. (—76 degrees Fahr.).

From the foregoing data it was possible to construct the diagrammatic treatment cycle shown in Fig. 33. This figure combines the results of the three methods, each point being marked with the

Table VII
Influence of Length of Time at —80° C. on Hardness and Permeability of Alloy No. 16

5.08% Nickel—17.60% Chromium
Brine-Quenched at 1090° C. (1995° F.)

Time at —80° C. (—112° F.)	Brinell Hardness	B/H for H-200
.5 hrs.	341	38.3
1.0	341	39.3
1.5	352	39.3
2.0	363	39.8
5.0	388	40.3
10.0	401	41.9
48.0	401	52.0

number corresponding to the method by which it was determined. The horizontal length of the breaks is proportional to the strength of the throw, and consequently to the intensity of the change. It is interesting to note how the Ar'' point is intensified by the quench. The intensity of the Ac_2 change also appears to be dependent upon the intensity of the Ar'' preceding it. Critical points upon steels 7 to 16 inclusive as determined by the three methods are given in Table VI.

c—*Influence of Rate of Cooling Upon Ar'':* A series of seven time-temperature curves made at different cooling rates, in which temperature is expressed as millivolts, is given in Fig. 34. The rates

Table VIII
Brinell Hardness After Liquid Air Treatments on Chromium-Nickel Alloys

Alloy No.	5	6	2	14	15	3	4	17
Nickel	4.03	5.06	5.23	5.36	5.54	5.99	7.04	9.20
Chromium	17.62	17.15	17.24	17.60	17.27	17.66	17.62	18.27
Brine-quenched at 1090° C.	418	286	286	171	185	255	241	116
Cold-treated at −180° C.	430	430	321	269	255	286	269	116
Cold-treated and drawn at 100° C.	430	430	321	269	255	286	269	116
Cold-treated and drawn at 200° C.	418	418	321	269	255	293	269	121
Cold-treated and drawn at 300° C.	418	418	302	269	241	277	269	121
Cold-treated and drawn at 400° C.	418	418	302	269	241	277	269	121
Cold-treated and drawn at 500° C.	387	388	302	248	235	269	269	121
Cold-treated and drawn at 600° C.	286	286	302	241	223	269	255	121
Cold-treated and drawn at 700° C.	311	321	302	269	248	269	255	121
Cold-treated and drawn at 800° C.	302	321	286	293	285	277	266	121

vary from 0.06 millivolts per minute to 2.60 millivolts per minute (21 degrees Cent. per hour to 16 degrees Cent. per minute). The depression of the critical point by rapid cooling is quite marked, and is shown logarithmically in Fig. 35. This is rather an important consideration in the practical treating of the alloy, since the change here is one from austenite to martensite, and suppression of the criti-

Table IX
Analyses of Iron-Nickel, Iron-Nickel-Silicon and Iron-Nickel-Molybdenum Alloys Investigated

Steel No.	Per Cent C	Mn	Si	P	S	Cr	Ni	Mo
18	0.05	0.64	0.13	0.010	0.025	0.02	24.73	....
19	0.05	0.57	0.15	0.010	0.026	0.03	26.78	....
20	0.05	0.67	0.10	0.009	0.026	0.03	28.00	....
21	0.04	0.43	0.13	0.009	0.031	0.04	30.09	....
22	0.10	0.24	1.46	0.009	0.026	0.03	25.91	....
23	0.05	0.22	3.83	0.012	0.019	0.03	24.93	....
24	0.16	0.27	3.91	0.011	0.021	0.15	24.97	....
25	0.06	0.14	3.40	0.011	0.027	0.11	24.47	....
26	0.07	0.62	4.00	0.011	0.028	0.11	23.71	....
27	0.12	0.15	0.11	0.013	0.020	0.03	24.95	4.02

cal point results in an increased proportion of retained austenite, necessitating a higher subsequent draw in order to secure the desired hardness. Usually it will be found desirable to cool at a moderately slow rate such as that employed upon the alloys shown in Fig. 21 to Fig. 25 inclusive., viz., 2 degrees per minute, in which case it is not necessary to draw above 100 degrees Cent. to secure maximum hardness.

d—*Effect of Time Element:* While cooling rate has an important bearing upon martensite transformation, duration of time at the low temperature also appears to have an important effect, particularly in the fast cooled specimens. Table VII shows hardness and perme-

Table X

Effect of Cold Treatment on Brinell Hardness of Nickel Steels

	Ni-Si Included for Comparison				
Alloy No.	18	19	20	21	23
Carbon	0.05%	0.05%	0.05%	0.04%	0.05%
Silicon	.....	.....	.....	.....	3.83
Nickel	24.73	26.78	28.00	30.09	24.93
As Forged	163	121	89	95	163
Cold-Treated —180° C.	293	321	302	255	418
Cold-Treated —180° C., Drawn 100° C.	321	302	293	255	418
Cold-Treated —180° C., Drawn 200° C.	321	302	293	255	444
Cold-Treated —180° C., Drawn 300° C.	302	302	293	255	460
Cold-Treated —180° C., Drawn 400° C.	302	293	286	241	555
Cold-Treated —180° C., Drawn 500° C.	286	286	277	235	512
Cold-Treated —180° C., Drawn 600° C.	149	166	166	174	302
Cold-Treated —180° C., Drawn 700° C.	143	140	131	126	149
Cold-Treated —180° C., Drawn 800° C.	143	140	131	121	131

ability figures upon specimens ½ inch round x 10 inches long, first brine-quenched at 1090 degrees Cent., (1995 degrees Fahr.) then cooled rapidly to —80 degrees Cent. (—112 degrees Fahr.) and held there for varying lengths of time. Cooling was done by immersing the specimen directly in a solution of acetone and dry ice, the low temperature probably being reached in less than 30 seconds.

e—*Effect of Treatments at Temperatures Lower Than —80 degrees Cent.:* While —80 degrees Cent. (—112 degrees Fahr.) represents the lowest temperature easily attainable on a commercial scale at the present time, it was nevertheless thought desirable to study the effect of lower temperatures such as those obtainable in liquid oxygen. Consequently eight steels ranging from 4.03 per cent nickel to 9.20 per cent nickel were brine-quenched from 1090 degrees Cent., cold treated to —180 degrees Cent. (—292 degrees Fahr.) in liquid oxygen and drawn at various temperatures. Hardness results are shown in Table VIII. Composition of Steel No. 17 is given in Table I.

The specimens for this work measured 1 x ¼ x 6 inches long, and were cooled directly in the liquid oxygen so that cooling was extremely rapid. Apparently nothing is gained in the 5.06 per cent nickel steel by going to the lower temperatures. Failure of the higher nickel steels to harden appreciably is noteworthy, although it should be noted that these steels showed greater gains in hardness after the liquid oxygen treatment than after the dry ice treatment as previously recorded, with the exception of alloy No. 17 containing 9.20 per cent nickel.

Table XI
Physical Properties of Nickel-Silicon Alloys Nos. 22 and 24 Cold-Treated in Liquid Oxygen to —180° C. (—292° F.)

Treatment	Zero P. L. Lbs./sq. in.	E. L. .0002″ Off Lbs./sq. in.	Ultimate Tensile Lbs./sq. in.	Elongation in 2″ %	Reduction of Area %	Brinell Hardness
Alloy No. 22 — 0.10 Per Cent Carbon—1.46 Per Cent Silicon—25.91 Per Cent Nickel						
As forged	45,000	52,500	97,000	48.7	68.2	182
As forged, cold-treated —180° C.	37,500	52,500	207,400	14.4	41.5	401
Brine-quenched at 1000° C.	12,500	15,000	86,600	53.5	70.4	163
Brine-quenched 1000° C., cold-treated —180° C.	30,000	47,500	194,200	16.4	50.3	387
Alloy No. 24 — .16 Per Cent Carbon—3.91 Per Cent Silicon—24.97 Per Cent Nickel						
As forged	45,000	52,500	100,400	49.3	68.6	187
As forged, cold-treated —180° C.	32,900	50,000	211,500	6.3	11.9	418
Brine-quenched at 1000° C.	12,500	17,500	88,800	55.7	71.0	163
Brine-quenched 1000° C., cold-treated —180° C.	31,000	52,500	203,900	15.2	35.7	387

Table XII
Physical Properties of Nickel-Silicon Alloy No. 23 After Cold Treating to —80° C. (—112° F.)

Treatment	Zero P. L. Lbs./sq. in.	E. L. .0002″ Off Lbs./sq. in.	Ultimate Tensile Lbs./sq. in.	Elongation in 2″ %	Reduction of Area %	Brinell Hardness
As forged	35,000	50,000	108,400	47.4	63.3	163
As forged, drawn 400° C.	42,500	55,000	108,900	45.8	66.8	149
As forged, drawn 600° C.	32,500	40,000	108,800	42.6	63.0	149
As forged, cold-treated —80° C.	17,500	32,500	160,200	21.5	51.9	340
As forged, cold-treated —80° C. drawn 400° C.	35,000	45,000	169,800	17.0	40.3	375
As forged, cold-treated —80° C., drawn 600° C.	45,000	55,000	121,900	33.6	66.4	228

Study of Iron-Nickel Alloys, Iron-Nickel-Silicon Alloys and Iron-Nickel-Molybdenum Alloys

Iron-Nickel Alloys

The effect of low temperatures on the physical properties of nickel steels has been studied by Chevenard[11]. However these tests were made at —190 degrees Cent. (—310 degrees Fahr.), and no observations are reported on change in properties after the nickel alloys returned to room temperature or after subsequent aging at higher temperatures. As previously noted, the circular of the Bureau

[11]Chevenard, *Revue de Metallurgie*, Vol. 19, p. 209.

Table XIII

Brinell Hardness and Specific Volume of Nickel-Silicon Alloys Nos. 22 and 24

Treatment	Alloy No. 22 .10% C—1.46% Si 25.91% Ni		Alloy No. 24 .16% C—3.91% Si 24.97% Ni	
	Brinell Hardness	Specific Volume	Brinell Hardness	Specific Volume
As forged	182	.128614	187	.128463
As forged, drawn at 400° C.	179	.128575	187	.128573
As forged, cold-treated —180° C.	401	.129156	418	.130018
As forged, cold-treated —180° C. drawn 400° C.	514	.129146	512	.129403
Brine-quenched at 1000° C.	163	.127496	163	.128268
Brine-quenched at 1000° C., cold-treated —180° C.	387	.129545	387	.132594
Brine-quenched at 1000° C., cold-treated —180° C., drawn 400° C.	514	.129184	512	.129290

of Standards No. 58[12] reports that the A_r point of iron-nickel alloys containing over 25 per cent nickel falls below room temperature, and that the A_r point of a 31.99 per cent nickel alloy occurs at —125 degrees Cent. (—193 degrees Fahr.). This circular also mentions that a number of Chevenard's alloys between 25.9 and 33.5 per cent nickel were found to be permanently elongated after cooling to —253 degrees Cent. (—423 degrees Fahr.).

From the results obtained on the cold treatment of the chromium-nickel alloys reported earlier in this paper, it was felt that the elongations reported by Chevenard were due to at least a partial transformation of austenite to martensite with the characteristic volume change. In order to determine this point, the effect of cold treatment on the hardness of a number of nickel alloys containing from 24.73 to 30.00 per cent nickel was determined. Complete analyses of these alloys are given in Table IX.

Tests were made on bars forged to ¾ inch square. The Brinell hardness after cold treating by immersing in liquid oxygen to —180 degrees Cent. (—292 degrees Fahr.) and drawing at various temperatures is given in Table X.

Alloy No. 19 containing 26.78 per cent nickel had a value of 321 Brinell which was the highest hardness obtained with these alloys after cold treating at —180 degrees Cent. (—292 degrees Fahr.). However all of these alloys showed an appreciable increase after cold treating. Alloy No. 18 containing 24.73 per cent nickel also increased in hardness to 321 Brinell after cold treating and drawing at 100 degrees Cent., and maintained this hardness up to 300

[12] "Invar and Related Nickel Steels," U. S. Bureau of Standards, Circular No. 58, 2nd edition, 1923.

Table XIV

Brinell Hardness and Permeability H-200 of Nickel-Silicon Alloys Nos. 25 and 26

Treatment	Alloy No. 25 .06% C—3.40% Si 24.47% Ni		Alloy No. 26 .07% C—4.00% Si 23.71% Ni	
	Brinell Hardness	Permeability H-200	Brinell Hardness	Permeability H-200
As forged	179	1.5	179	1.5
As forged, cold-treated —180° C.	418	48.2	402	43.2
As forged, cold-treated —180° C. drawn 100° C.	430	48.2	402	43.2
As forged, cold-treated —180° C. drawn 200° C.	444	48.2	430	43.7
As forged, cold-treated —180° C. drawn 300° C.	460	48.2	444	43.7
As forged, cold-treated —180° C. drawn 300° C.	532	50.7	514	46.2
As forged, cold-treated —180° C. drawn 500° C.	495	48.7	477	45.7
As forged, cold-treated —180° C. drawn 600° C.	311	24.2	302	21.7
As forged, cold-treated —180° C. drawn 700° C.	166	1.5	163	1.5
As forged, cold-treated —180° C. drawn 800° C.	159	1.5	159	1.5

degrees Cent. (570 degrees Fahr.). This alloy exhibited the same characteristic as the 18.00 per cent chromium-5.00 per cent nickel alloys previously investigated. All the other iron-nickel alloys decreased gradually in hardness as the drawing temperature increased up to 600 degrees Cent. (1110 degrees Fahr.). At this temperature the alloys became austenitic again with characteristic low hardness values.

Iron-Nickel-Silicon Alloys

Alloy No. 23 containing 24.93 per cent nickel and 3.83 per cent silicon was included in the cold treatment work on the nickel alloys. The results of the cold treatment and subsequent drawing on this alloy are given in Table X. This alloy became much harder than any of the nickel alloys containing only the normal amounts of silicon. Subsequent drawings increased the hardness values gradually until a maximum of 555 Brinell after drawing at 400 degrees Cent. (750 degrees Fahr.) was reached. Alloy No. 18 containing practically the same nickel content but 0.13 per cent silicon had a maximum hardness of only 321.

The results of cold treating and drawing alloy No. 23 were sufficiently interesting to warrant a more complete investigation of the iron-nickel-silicon alloys. Accordingly the following information was obtained on a number of alloys containing between 1.50 and 4.00 per cent silicon:

1—Physical properties
2—Brinell hardness and specific volume
3—Permeabilities
4—Microstructures

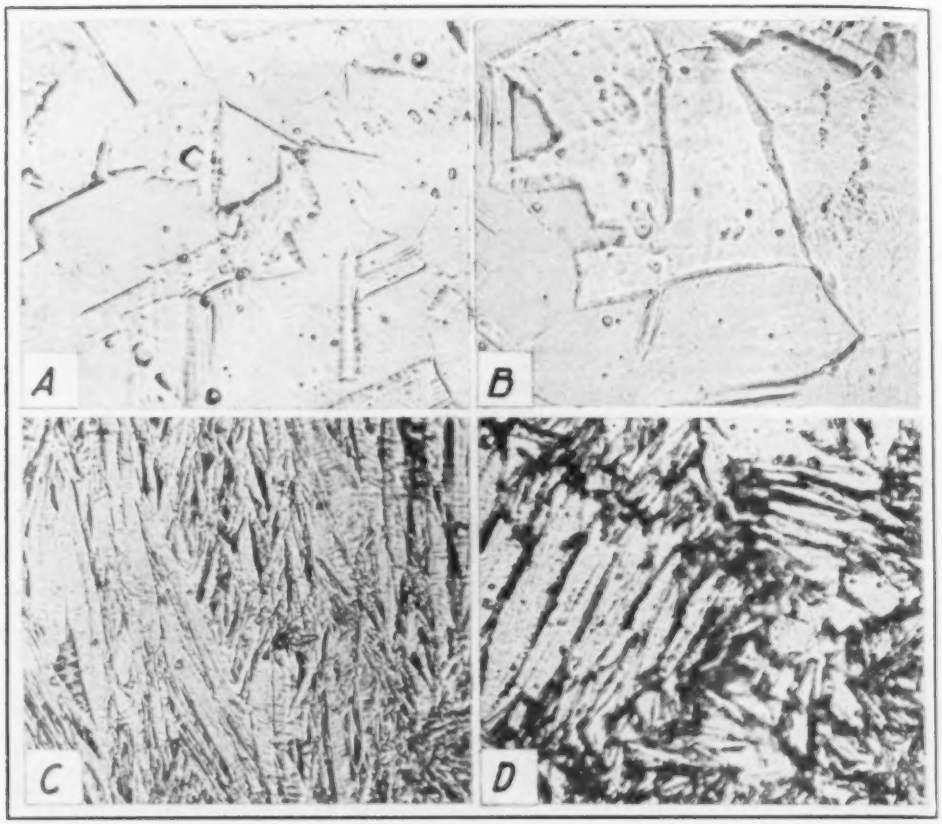


Fig. 36—Steel Containing 23.71 Per Cent Nickel, 4.00 Per Cent Silicon. A—As-forged; B—As-forged and Drawn at 400 Degrees Cent. C—As-forged and Cold-treated at —180 Degrees Cent.; D—As-forged and Cold-treated at —180 Degrees Cent., and Drawn at 400 Degrees Cent. All Micrographs × 1000. Etched in Acid Ferric Chloride and H_2O_2.

1—Physical Properties: Physical properties on alloys at either extremity of this group are given in Table XI. The increase in ultimate strength and hardness with corresponding decrease in elongation and reduction of area after cold treating to —180 degrees Cent. (—292 degrees Fahr.) in liquid oxygen is obvious. Cold treating after brine quenching at 1000 degrees Cent. (1830 degrees Fahr.) however made a considerable improvement in both elongation and reduction of area, with approximately the same ultimate strength. Tensile tests after cold treating and drawing at 400 degrees Cent. (750 degrees Fahr.) were not successful, since after this treatment these alloys were over 500 Brinell.

The physical properties of alloy No. 23 after the more commercial form of cold treatment at —80 degrees Cent. (—112 degrees Fahr.) are given in Table XII. Specimens instead of being im-

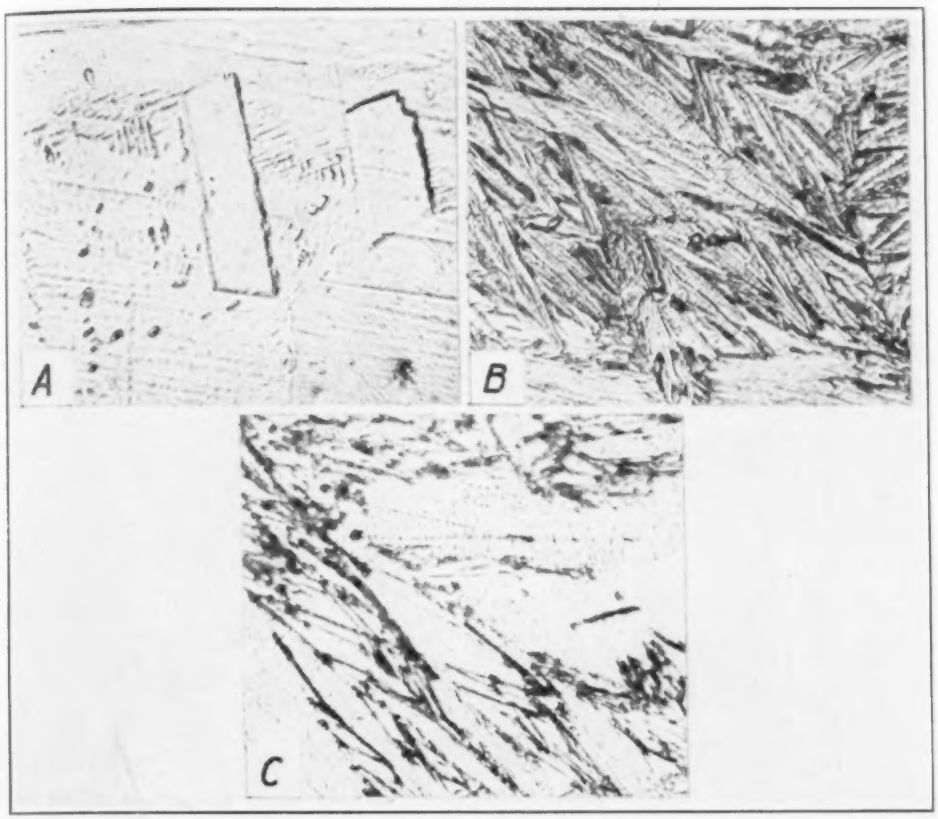


Fig. 37—Steel Containing 23.71 Per Cent Nickel, 4.00 Per Cent Silicon. A—Water-quenched from 1000 Degrees Cent.; B—Water-quenched from 1000 Degrees Cent., and Cold-treated at —180 Degrees Cent.; C—Water-quenched from 1000 Degrees Cent., Cold-treated at —180 Degrees Cent., and Drawn at 400 Degrees Cent. All Micrographs × 1000. Etched in Acid Ferric Chloride and H_2O_2.

mersed in liquid oxygen at —180 degrees Cent. (—292 degrees Fahr.) were treated in a solution of acetone and dry ice at —80 degrees Cent. After this cold treatment the tensile strengths were appreciably increased with fairly good ductility. Specimens as forged and drawn at 400 and 600 degrees Cent. (750 and 1110 degrees Fahr.) without cold treatment are included for comparison. Apparently the transformation in this alloy has only begun at —80 degrees Cent., and is completed between this temperature and —180 degrees Cent.

2—Brinell Hardness and Specific Volume: Brinell hardness and specific volume determinations were made on alloys Nos. 22 and 24. Specimens were cold treated at —180 degrees Cent. both as forged and as quenched from 1000 degrees Cent. The specific volume determinations were made on specimens ½ inch in diameter and 1 inch

Table XV
Brinell Hardness and Permeability H-200 of Nickel-Molybdenum Alloy No. 27

0.12 Per Cent Carbon—4.02 Per Cent Molybdenum—24.95 Per Cent Nickel

Treatment	Brinell Hardness	Permeability H-200	Izod Foot Lbs.
As forged	170	1.7	..
As forged and cold-treated —180° C.	302	17.3	36
As forged, cold-treated —180° C. and drawn 100° C.	302	17.3	..
As forged, cold treated —180° C. and drawn 200° C.	321	17.8	28
As forged, cold-treated —180° C. and drawn 300° C.	332	28.1	30
As forged, cold-treated —180° C. and drawn 400° C.	387	28.5	22
As forged, cold-treated —180° C. and drawn 500° C.	332	27.7	27
As forged, cold-treated —180° C. and drawn 600° C.	241	8.3	..
As forged, cold-treated —180° C. and drawn 700° C.	187	4.2	..
As forged, cold-treated —180° C. and drawn 800° C.	163	4.2	..

long and the hardness values made on specimens ¼ x 1 x 6 inches long. Table XIII gives the data obtained on these tests. The appreciable increase in hardness and specific volume is of course due to the transformation of austenite to martensite. It is interesting to note in passing that apparently 1.46 per cent silicon is sufficient to completely change the character of a 25 per cent nickel alloy and to obtain properties similar to those found with the higher silicon alloys.

3—Permeabilities: The Brinell hardness and permeabilities of alloys Nos. 25 and 26, containing 3.40 per cent silicon and 4.00 per cent silicon respectively, were obtained after cold treating at —180 degrees Cent. and drawing from 100 to 800 degrees Cent. in 100 degree intervals. These data are given in Table XIV.

The bars used for the magnetic test were ½ inch in diameter and 10 inches long. Hardness determinations were made on the same bars. The increase in permeability after cold treating corresponds to the increase in hardness. Both increased gradually to 400 degrees Cent. where a maximum was reached. There was a sharp drop in both hardness and permeability between 600 and 700 degrees Cent. where the alloys returned to austenite.

4—Microstructures: The microstructures of alloy No. 26 containing 23.71 per cent nickel and 4.00 per cent silicon are given in Figs. 36 and 37. Fig. 36-A shows the normal austenitic structure of this steel in the forged condition. Fig. 36-B after drawing at 400 degrees Cent. (750 degrees Fahr.) without intermediate cold treatment shows no change. In Fig. 36-C the coarse martensite obtained after cold treating at —180 degrees Cent. (—292 degrees Fahr.) is shown. Drawing at 400 degrees Cent. after cold treat-

ing at —180 degrees Cent. darkens the martensite needles considerably as shown in Fig. 36-D. Brine quenching at 1000 degrees Cent. (1830 degrees Fahr.) increased the grain size of the austenite considerably as shown in Fig. 37-A. Figs. 37-B and 37-C show the coarse martensite obtained after cold treating at —180 degrees Cent. and cold treating followed by drawing at 400 degrees Cent. respectively.

Iron-Nickel-Molybdenum Alloys

The extremely coarse martensite developed in the nickel-silicon alloys made them very brittle. Since the size of the martensite was dependent upon the size of the original austenitic grains, the addition of elements such as vanadium or molybdenum that might decrease the grain size was considered.

The hardness, permeability and Izod impact values were obtained on alloy No. 27, containing 24.95 per cent nickel and 4.02 per cent molybdenum. The data obtained on these tests are given in Table XV. The molybdenum apparently lowered the A_r point so that at —180 degrees Cent. (—292 degrees Fahr.) only part of the transformation had taken place. However it is interesting to note that an Izod impact of 22 foot-pounds was obtained at the maximum Brinell hardness which was 387 after drawing at 400 degrees Cent.

Summary and Discussion

Preliminary tests upon a series of steels containing approximately 18.00 per cent chromium with nickel varying up to 9.20 per cent indicated that the alloys containing approximately 5.00 per cent nickel possessed borderline characteristics, lying between the so-called austenitic steels and the martensitic or pearlitic steels. Such characteristics imply the suppression of the A_r transformation to a point below room temperature, and it was consequently found that alloys containing approximately 5.00 per cent nickel could be considerably hardened by cooling to a low temperature such as obtained in dry ice.

A complete study of the physical properties of both the 4.00 and 5.00 per cent nickel alloys after various treatments, some of which included a cooling treatment to —80 degrees Cent. (—112 degrees Fahr.), developed several points which deserve careful thought, particularly in connection with the 5.00 per cent nickel al-

loy. In this respect, the great increase in hardness following cold treatment and suitable drawing is outstanding. This increase is accompanied by an increase in ductility with no drop in Izod values which suggests some very interesting practical applications, particularly in view of the fact that parts may be hardened by this method without discoloration of the surface. The increase in specific volume and permeability indicates a definite transformation of austenite. The marked improvement in machinability produced by the cold treatment followed by a suitable draw is noteworthy and undoubtedly results from the further break-down of martensite into the softer constituents. Microscopic studies confirm both these observations. Specimens given similar treatments, however, omitting the refrigeration at —80 degrees Cent. (—112 degrees Fahr.), remain practically unchanged, indicating definitely that the low temperature cooling is essential. Attention is again called to the excellent physical properties at elevated temperatures up to 400 degrees Cent. (750 degrees Fahr.) and to the resistance to corrosion in salt spray. There is nothing whatever to indicate that the cold treatment has impaired the corrosion resisting properties, and in fact there is reason to believe that it actually has improved them. These properties suggest other practical applications.

Further studies of the effect of small variations in nickel content indicated a maximum of 5.10 per cent nickel for the most effective hardening, with a permissible range of approximately 4.70 to 5.10 per cent nickel. Subsequent work upon critical points, effect of cooling rate, etc., was therefore conducted upon an alloy containing 5.08 per cent nickel.

For the accurate determination and control of low temperatures required in the determination of the thermal as well as magnetic points, it was necessary to design a thermocouple of extreme sensitivity and a low temperature muffle. Both of these proved entirely practical and could undoubtedly be used in some modified form in production work.

The critical points observed probably lend themselves to various interpretations. The authors suggest that the heating and cooling points observed in the vicinity of 600 degrees Cent. represent A_{c_2} and A_{r_2} respectively, since they are strictly magnetic points and show practically no lag. The thermal point observed below room temperature is believed to be A_r'', corresponding to the change observed in quenched carbon steels at approximately 250 degrees Cent.

The alloys are obviously too sluggish to permit the A_r' transformation. The apparent absence of a thermal point at A_r'' upon the "as-rolled" alloys is probably due to the presence of considerable martensite in these specimens, resulting in a further change which is too gradual to be detected by the thermocouple. In contrast to this, the fully austenitic specimens transform so rapidly that distinct under-cooling is observed in the slowly cooled specimens. Dilatometric curves would undoubtedly throw some light upon the occurrence of these points as observed in specimens treated to various initial conditions. As would be expected, only the alloys of sufficiently low nickel content to exhibit these low critical points were found to respond to cold treatment.

No advantage was shown by cooling the 5.08 per cent nickel steel to liquid oxygen temperature, and apparently the dry ice temperatures are sufficiently low for all practical purposes.

Review of previous work indicated that A_r transformations were possible on other alloys, particularly the iron-nickel, upon cooling to temperatures below atmospheric. However no results of the physical properties or hardnesses after cold treating and returning to room temperature are recorded. Accordingly a group of alloys containing from 24.73 to 30.00 per cent nickel were cold treated at —180 degrees Cent. (—292 degrees Fahr.) in liquid oxygen. Appreciable increases in hardness were obtained.

In the preliminary work an alloy containing 3.83 per cent silicon and 24.93 per cent nickel was found to exhibit a much greater increase in hardness than an alloy of practically the same nickel content with normal silicon. This is particularly noticeable after drawing the cold treated specimens at 400 degrees Cent. The increase in tensile properties after cold treating corresponds to the increased hardness obtained. The microscopic study, specific volume and permeability determinations further confirm the transformation of austenite to martensite. The maximum hardness obtained after cold treating at —180 degrees Cent. (—292 degrees Fahr.) and drawing at 400 degrees Cent. (750 degrees Fahr.) is probably due to the breakdown of retained austenite. It is interesting to note that in this respect these alloys behave as the rapidly cooled specimens of the chromium-nickel steels containing approximately 5.00 per cent nickel.

The replacement of the silicon with molybdenum in a 25 per cent nickel steel resulted in the suppression of the A_r point. Conse-

quently only part of the transformation had taken place at —180 degrees Cent. (—292 degrees Fahr.) with the corresponding smaller increase in hardness.

Conclusion

The field of treatment at low temperatures is one of such breadth that of necessity the authors have omitted a detailed discussion of many phases of the subject, and quite likely have neglected many of its possibilities. While the paper is therefore offered in a sense as a progress report, it is hoped that some of the points touched upon may prove sufficiently promising to invite a more detailed study by other investigators.

Acknowledgment

The authors are pleased to acknowledge the helpful interest and support of Messrs. J. H. Parker and B. H. DeLong of The Carpenter Steel Company during the progress of this investigation, and the assistance of the various members of the metallurgical staff who were directly engaged in the experimental work.

DISCUSSION

Written Discussion: By John A. Mathews, vice-president, Crucible Steel Company of America, New York City.

The large number and very excellent quality of the papers presented this week dealing with corrosion resistant steels, and the exhibit of products made from them at the exposition, takes my mind back to a time when two struggling young societies had just merged to become the American Society for Steel Treating, which was holding its first convention and exposition in Philadelphia in 1920. At that exposition the Crucible Steel Company of America first showed to the American public a considerable series of these steels in various forms and shapes. A number of them that had been "preserved" in strong nitric, acetic, phosphoric and caustic solutions for a period of weeks or months attracted much attention. At this convention, Mr. Charles M. Johnson, who was responsible for these products, presented a paper which appears in Volume I of our Transactions. The products were produced and studied during the period from 1917 up to the time of the exposition.

It is customary for parents to name their children rather promptly but in this instance the progeny was so numerous that individual names were not provided until after Mr. Johnson's paper had been given. Then the generic name Rezistal was given to them and the individual varieties were numbered. In his paper they were referred to as Grade 2, 3, 4, etc. It so happens that Grade 2 was what we now call Rezistal No. 2 and is probably the first so-called 18-8 steel

produced in this country. It was made in 1917. His other grade numbers corresponded to our Rezistal numbers as used today. At the time of his earlier experiments these steels were melted in crucibles and without the use of low carbon ferrochromium which we have today and without the ability to decarburize the material as can be done in electric furnaces. Consequently, most of these earlier steels were rather high in carbon. The point I wish particularly to make is, however, that this very early paper makes mention of most all the subjects we are discussing today. Mr. Johnson describes how Grade 2 (18-8) may become magnetic by long holding at around 1200 to 1300 degrees Fahr. but loses its magnetism at a somewhat higher temperature and that it can be again made magnetic by reheating in the 1200 degrees Fahr. range.

He mentions that other steels are not thus affected. This paper makes no mention of the words austenite or austenitic but, obviously, the steels which became magnetic were the border line types of alloys and not the more stable austenitic alloys. He describes and illustrates the effect of elevated temperatures up to 2400 degrees Fahr. on grain size, tensile properties and impact resistance. He gives the tensile qualities of very fine wire. He describes the effect of cold treatment on some of his products in liquid air and apparently the ones on which he tried liquid air were the stable austenitic varieties. He describes the high temperature annealing for forming operations but, apparently, did not experiment with reference to the effect of variable temperature treatments on corrosion resistance. We now know a lot that we did not know then about the still earlier work of Dr. Strauss at the Krupp Works. Nevertheless, Mr. Johnson produced similar, but not identical, grades of products quite independently. It should be remembered that his first experiments were actually made during the war period and that his paper and our exhibit preceded the issuing in this country of the Strauss patents.

In regard to the paper by Messrs. Luerssen and Greene and also the paper by Messrs. Krivobok and Gensamer, presented before the American Institute of Mining Engineers, we note that all of these workers draw attention to the hardening effect of very low temperatures on certain of the corrosion-resistant steels. It is not stated just how generally this effect may be obtained. Messrs. Luerssen and Greene hardened their steels in a constant temperature of 1090 degrees Cent. and apparently did not study the effect of variable quenching temperatures prior to the cold treatment on the group with which they worked. The number of products which may be made to respond to the cold treatment is rather wide and the effect does vary depending upon the temperature of quenching. Not only the carbon-chromium-nickel ratio but other added metals control this behavior. In other words, the possibilities with these so-called border line steels is (1) either to harden or soften by quenching—depending upon the temperature (2) after such treatment either to harden or not harden by certain cold treatments and (3) in some cases to materially harden by precipitation hardening at elevated tempering temperatures. For example, a steel of 0.33 per cent carbon, 7.47 per cent nickel and 12.64 per cent chromium, as quenched from 1800 degrees Fahr. showed a Rockwell C hardness of 30. After cold treatment in dry ice this increased to 47. The same steel after a 2100 degrees Fahr. quench showed 10 Rockwell C, and after the cold treatment had only increased to 11. A series of steels (some-

what analogous to the authors', but higher in carbon and lower in chromium), was very uniform except for the nickel content—the carbon being 0.40 and the chromium 16.5 per cent. The first of these showed 4.14 per cent nickel and by direct quenching from 1800 degrees Fahr. showed 48 Rockwell C—after cold treatment, 49. After a 2100 degrees Fahr. quench it showed 28 and 29, respectively. The second modification with 4.82 per cent nickel, hardened at 1800 degrees Fahr., gave Rockwell 43 and after cold treatment, 49. After the 2100 degrees Fahr. quench it showed 24 and after cold treatment 25. The third number of this group with 5.91 per cent nickel showed Rockwell 37 after quenching from 1800 degrees Fahr. and 47 after cold treatment. After the high quench it showed Rockwell 23 as quenched and after the cold treatment. It will be noted that as the nickel increased in this series the initial hardening capacity decreased from both the low and high quench. In other words, the highest nickel content was sufficient to bring about considerable austenite on both the low and high quench. It would appear that the austenite following the low quench was more unstable than the austenite after the high quench, for it is transformed to produce great increase in hardness, while the austenite resulting from the high quench does not seem to be transformed, at least at the temperature of dry ice.

Referring again to the first steel mentioned with 12.64 per cent chromium and 7.47 per cent nickel which showed marked hardening after a low quench and cold treatment but not after the high quench, it is interesting to note that the addition of 2.5 per cent tungsten to this same steel destroyed its capacity for rehardening after either the high or low quench. As a matter of fact, its initial hardness was less after the low quench and greater after the high quench than the steel without tungsten. The series of steels in which the nickel varied between 4.14 and 5.91 per cent, both as-rolled and after various quenches, showed a considerable capacity to harden at various tempering temperatures between 1000 degrees Fahr. and 1600 degrees Fahr.—varying from 2 to 15 points Rockwell C.

The subject is a very interesting one and the field of study is much broader than is indicated in the paper under discussion, but the authors are to be congratulated upon their very excellent work insofar as the range of steels which they considered is concerned.

Written Discussion: By H. S. Rawdon, chief metallurgical department, U. S. Bureau of Standards, Washington, D. C.

It is certainly a pleasure to read the report on such a well executed piece of work as this one. Many metallurgists have at times studied the effect of cooling on austenitic steels or other alloys in a structurally unstable state. Usually such attempts have been incidental to other objectives, however. The present work is outstanding in the comprehensive and systematic manner in which it has been planned and executed and particularly in the endeavor made to make the results commercially practicable. The work has been so well planned that, in large measure, any questions that might ordinarily arise have been forestalled.

The results have clearly shown that nickel-chromium steels of the proper composition, that is "marginal austenitic" compositions, do respond to the cold treatment with such marked improvement of their properties that it would seem there could be no reasonable doubt that the method will prove feasible and useful from the commercial standpoint. Likewise, the results show the limitations of

this method of treatment. It will be a source of real regret to metallurgists in general that the widely used "18 and 8" alloy steel does not respond to this treatment. The field of usefulness of the marginal austenitic steel with 5 per cent of nickel and 18 of chromium is decidedly narrower than that of the "18 and 8" alloy. In particular, does this apply when corrosion-resistance is the decisive factor, for this property decreases as the nickel content is lowered below the usual 8 per cent, the assumption being made, of course, that no other compensating change in composition is made.

The writer considers that the results given by the authors showing the relative corrosion-resistive properties of the various alloys are not discriminating enough in this respect. This criticism should be taken as applying to the general method used rather than the authors' application of the method in this particular case. The salt spray test is widely used as an acceptance test for alloys of the "18 and 8" type, although it is generally recognized that it is far from being a satisfactorily discriminating test method. The main criticism of the method is that it is not severe enough. Only those materials whose corrosion-resistive properties are decidedly low are rejected on the basis of the results. A more suitable method for determining the corrosion-resistive properties of the stainless class of steels is one of the crying needs of the industry.

Any one who did not examine into the matter very far might conclude that inasmuch as the alloy with 5 per cent nickel after certain treatments withstood 100 hours in the salt spray test without rusting, it should be accepted as equivalent in its corrosion-resistive properties to an "18 and 8" alloy passing the same test, since this requirement has come to be recognized as one of which the latter material must meet. This may be far from the truth, however.

The suggestion has been made that perhaps the salt spray test can be intensified sufficiently so as to make its results more dependable and discriminating for uses such as the present. A few tests, admittedly preliminary in scope, and limited in number, made at the Bureau of Standards with a solution of sodium chloride to which an oxidizing agent (hydrogen peroxide) had been added have given some promising results along this line. Defects were revealed which were entirely unsuspected on the basis of salt spray tests alone. The statement may well be repeated that a suitable discriminating accelerated testing method for the stainless class of steel is one of the crying needs of the industry.

Written Discussion: By E. S. Davenport and R. H. Aborn, associated with research laboratories, U. S. Steel Corporation, Kearny, N. J.

This paper is one of peculiar interest to us in view of the investigations in our laboratory on the inordinately rapid transformation rates of carbon steels in the zone from room temperature to 150 degrees Cent. (300 degrees Fahr.). Due to the nature and content of alloying elements this zone is found to be shifted to the region below room temperature with an apparently retarded rate. This is indeed a very fruitful field of investigation, and one in which our knowledge of the true nature of these alloy steels can only be broadened by intensive work in rather narrowly limited composition regions, such as undertaken by the authors in the present instance.

The paper contains further welcome evidence of the fact that the so-called Ar and Ac "points" are not, strictly speaking, fixed points at all, but are values

dependent upon the conditions under which they are determined. The only true critical points are those which are determined under equilibrium conditions. This has been repeatedly brought to our attention within the past two years in the course of investigations on many types of steel at our laboratory.

The author's belief that small variations in carbon content may exert an important influence on the position of the boundary line between the wholly austenitic field and the mixed field of austenite and ferrite is of course well confirmed in the alloys of adjoining composition on the side of higher nickel content, such as the "18-8" type. Apparently the authors' alloy containing 9.20 per cent nickel failed to respond to any treatment given, including liquid air. It would be interesting to know, however, whether the authors regard the permeability data on the 7.04 per cent nickel alloy as indicating the production of an appreciable amount of martensitic ferrite in the —75 degrees Cent. quench, and also whether they have obtained any magnetic data on this alloy in connection with the liquid air treatment.

When employing a cooling rate of 2 degrees Cent. per minute as suggested, it would be of interest to know if the authors have found as desirable mechanical properties after any drawing treatment as those shown in the 400 degrees Cent. (750 degrees Fahr.) draw in Table III where the low-temperature cooling rate was some five times faster.

In the chromium-nickel steels chosen by the authors, the A_3 transformation temperature range (ferrite $\leftrightarrow$ austenite) very likely overlaps the A_2 range. May it not be possible that the magnetic changes which the authors refer to as Ac_2 and Ar_2 are in reality due to both A_2 and A_3 changes? In fact, the marked decrease in magnetic intensity on cooling (cf. Fig. 28) gives some basis for the view that the observed effect on heating is due primarily to the transformation of ferrite to austenite, which on cooling is largely irreversible due to sluggishness. If the A_2 change alone were involved, the intensities on heating and cooling should be substantially equal.

The authors' paper represents a vast amount of work carried out with admirable skill and care, but it is clear that only a beginning has been made in this comparatively new field of low temperature treatment. From the very nature of the subject, even a modest program involves an immense multiplicity of observations. For example, information on the actual rates of transformation at these low temperatures is still meager. The transformation rates of carbon and low alloy steels in the vicinity of room temperature would lead us to expect very rapid transformation at lower temperatures; however, the low atomic mobility at such temperatures, coupled with the inherent sluggishness of these "border-line" alloys, might well cause the reactions to be quite slow in reaching completion. It might even prove true that the reactions would proceed to a definite extent beyond which extremely low temperatures cause no further change. The use of dilatometric methods, as suggested by the authors, holds much promise. It is hoped that with the experience already acquired the authors will see fit to continue their valuable investigations in the immediate future.

Written Discussion: By A. B. Kinzel, associated with the Union Carbide and Carbon Research Laboratories, Inc., Long Island City, N. Y.

This work by Messrs. Luerssen and Greene is an extremely valuable, well

thought out, admirably executed, thorough investigation of sub-room temperature transformations in alloys which are of distinct commercial interest. The methods used are ingenious, and the results appear to be reliable.

In the cold treatment, severe temperature gradients have been set up, so that the strains accompanying these could produce the same effect as cold working. It is possible that this condition may be one of the factors involved in producing the transformation at the low temperature. It is hard to conceive of the occurrence of transformations at low temperatures in alloys such as those containing high chromium without some additional force to increase the atomic mobility. Possibly, the initial cold working produced by temperature gradients starting the transformation is supplanted by the strain set up in the transformation itself, thus producing a progressive transformation. The striking undercooling on some of the specimens is in accord with this view. The writer believes that the authors' interpretations of the critical point of curves are most probable.

The authors point out the possibilities of hardening without scaling. However, from a practical standpoint it would seem that such treatment would be quite cumbersome, except for small pieces or wire. The establishment of a comparatively narrow range of border-line alloys at 4.70 to 5.10 per cent nickel with very slight variations in chromium content, indicates the extreme sensitivity of the method. It also indicates that it would be rather difficult to apply commercially because of the close control of analysis which will be necessary in the "18-5" type alloy. Data given on other alloys which are not of the stainless group indicate the possibilities of wider range in analysis.

Messrs. Luerssen and Greene have certainly increased our knowledge with respect to this comparatively unexplored phase of metallurgy, and deserve our fullest appreciation.

Oral Discussion

V. N. KRIVOBOK:[1] I wish to take this opportunity to state that the paper by Messrs. Luerssen and Greene deserves a great deal of attention. It is easy to make flattering remarks, but the best proof of the value of the paper lies in the interest it arouses. I had the privilege to know about this work while it was in progress. The remark which was made today during the discussion and which has a direct bearing on the composition of these steels, deserves particular attention. The range of composition of the steels of chromium-nickel stainless type that will respond to cold treatment is not so narrow as indicated in the paper. The hardening brought about by cold immersion depends very much on carbon content, as we have found out pursuing similar investigation. The authors will undoubtedly agree with me.

I am in disagreement, I am sorry to say, with the interpretation of the critical point, which is taken to be the A_2 point as stated in the paper. I was glad to hear Mr. Luerssen say in his presentation that it is probably a combination of points. First of all the steel in question is hypereutectoid, and the same transformation that is described in the paper can be determined by other

[1]Metallurgist, Bureau of metallurgical research and professor of metallurgy, Carnegie Institute of Technology, Pittsburgh.

methods, notable among which is the dilatometric one, thus indicating that it could not be the A_2 point.

I am also somewhat in disagreement with the statement that the effect of time at low temperature is quite important. In the work which was pursued in our laboratories we found repeatedly that it is necessary to cool the alloy down to a certain temperature in order to start the transformation. If the temperature remains unchanged the transformation will proceed just so far and, at least within reasonably long time, no further changes will be observed. Slight lowering of the temperature results in further progressive transformation. It is illustrated by the volumetric changes rather than by measuring hardness.

I am fully convinced that this work opens a large field, and I was glad to hear from Dr. Mathews that it might be very well applied to other steels, such, for example, as high speed steel.

Authors' Closure

Dr. Mathews' discussions are always welcome and to the point. It is a fine thing to have in our organization some one to act as a sort of balance wheel, and to help show us the way when we get into new and unexplored fields.

With regard to his remarks on the effect of quenching temperature upon the ultimate properties, we have investigated this field to some extent. Following is a table showing Brinell hardness after quenching at temperatures ranging from 1500 to 2000 degrees Fahr., and Brinell hardness of these same pieces after cold treating:

Quenching Temperature	Brinell As Quenched	Brinell As Cold Treated
1500 degrees Fahr.	321	321
1600 degrees Fahr.	341	341
1700 degrees Fahr.	363	375
1800 degrees Fahr.	363	429
1900 degrees Fahr.	352	401
2000 degrees Fahr.	277	444

As indicated by Dr. Mathews, quenching temperature seems to have quite an effect. It will be noted, however, that between quenching temperatures of 1800 and 2000 degrees Fahr., the final hardness results are fairly uniform.

Dr. Mathews' results on the 16 per cent chromium and 0.40 per cent carbon with variable nickel content are very interesting and undoubtedly add to our information on the subject.

The discussion by Messrs. Davenport and Aborn indicates a very thorough study of the paper, and we greatly appreciate their suggestions. The change in permeability on the 7.04 per cent nickel steel is so slight that we have not attached any significance to this change. Neither have we investigated the effect of a liquid air treatment on this alloy except as regards hardening. No difference in Brinell hardness between −75 degrees Cent. and liquid air temperatures has been found.

Their point with regard to the effect of cooling rate on subsequent physi-

cal properties is very well taken, and we are at present making a study of this variable. Another point well taken is that in connection with the possibility of the overlapping of the A_2 and A_3 points. The question could be more readily answered if we knew exactly what the eutectoid composition of the alloy really is. We have generally assumed that the alloy is hypereutectoid, and that the two points are, therefore, merged.

We are in accord with Messrs. Davenport and Aborn's view with regard to the sluggishness of these alloys. This is well shown in Fig. 34 in the paper in which the depression of the critical point is shown to be quite marked with increase in cooling rate. It is gratifying that so many of our views on the principles governing the behavior of these alloys agree so closely.

We agree with Mr. Kinzel that it is somewhat difficult to conceive structural changes actually taking place in these alloys at such extremely low temperatures. However, his stress theory does not appear to be tenable, since our best results were obtained by extremely slow cooling in which cases the thermal gradient was practically nil. The point is one which will bear further investigation.

We are indeed grateful to Dr. Rawdon for his discussion. We agree with his statement in regard to the exclusive use of the salt spray test as a method of measuring corrosion-resistance. We have experimented with supplementary tests and have more or less standardized on the one described by W. R. Huey, particularly for the chromium-nickel alloys. This test employs 65 per cent boiling nitric acid for five 48-hour periods. The corrosion rate is reported in inches per month. Some of the results on "18-5" alloy as compared to ordinary "18-8" are as follows:

	C	Cr	Ni
18-5	0.08 per cent	17.60 per cent	5.08 per cent
18-8	0.03 per cent	17.58 per cent	8.09 per cent

	18-5 In/Mo.		18-8 In/Mo.
Quenched 1100 degrees Cent. (2010 degrees Fahr.)	0.002261	Quenched 1100 degrees Cent. (2010 degrees Fahr.)	0.001868
Quenched 1100 degrees Cent. C. T. −80 degrees Cent. (−112 degrees Fahr.)	0.002162		
Quenched 1100 degrees Cent. C. T. −80 degrees Cent. Drawn 600 degrees Cent. (1110 degrees Fahr.)	0.004243	Quenched 1100 degrees Cent. Drawn 600 Degrees Cent. (1110 degrees Fahr.)	0.03690
Quenched 1100 degrees Cent. C. T. −80 degrees Cent. Drawn 800 degrees Cent.	0.003505	Quenched 1100 degrees Cent. Drawn 800 degrees Cent. (1470 degrees Fahr.)	0.003768

We greatly appreciate Dr. Krivobok's remarks, and in turn have had the opportunity to follow the very interesting dilatometric work carried out in his laboratory.

The A_2 point discussed in the paper is undoubtedly a combination of points

as suggested by Dr. Krivobok, and beautifully illustrated in his dilatometer curves.

With regard to the effect of holding time upon the transformation at low temperatures, we also observed the phenomenon mentioned by Dr. Krivobok. The specimens shown in Table V were all held four hours, which we found to be the maximum time necessary for completion of the transformation on slowly cooled specimens. However, after rapid cooling the transformation was not complete after holding five hours, and evidently a holding time of ten hours was necessary to complete the hardening. This is shown in Table VII.

MAGNETIC AND MECHANICAL HARDNESS OF DISPERSION HARDENED IRON ALLOYS

By K. S. Seljesater and B. A. Rogers

Abstract

The effect of dispersion or age hardening upon the magnetic properties of a number of carbon-free binary, ternary, and quaternary iron alloys has been investigated.

Binary alloys of iron with tungsten, molybdenum, beryllium, and titanium all exhibit a marked increase in coercive force, accompanied by a rise in residual magnetism, as the temperature of the aging treatment is raised. In some cases the increase in coercive force occurs simultaneously with the rise in hardness value, while in others, notably the iron-titanium alloys, the magnetic properties do not change appreciably until the hardness readings have gained considerable or even reached their maximum value. Both hardness and coercive force pass through maximum values. The binary alloy containing 23.4 per cent molybdenum attained a coercive force of over 200 gilberts per centimeter.

Among the ternary group, the iron-tungsten-cobalt combination is of greatest interest. Unlike magnet steels, these alloys do not attain maximum mechanical and maximum magnetic hardness under the same treatment, but experience a minimum of coercive force as the hardness passes through maximum value.

Introduction

FUNDAMENTAL knowledge pertaining to dispersion hardening of carbon-free iron alloys is at present rather incomplete. Credit is due to W. P. Sykes for his thorough exploration of the iron-tungsten and iron-molybdenum systems and for the discovery of dispersion or "age hardening" in iron alloys. Such hardening results from an increasing solid solubility with increasing temperature of some constituent and the ability to suppress precipitation by rapid cooling. According to the generally accepted theory, as quenched from a high temperature the alloy consists of a supersaturated solution, and upon

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aging at a suitable temperature this constituent is precipitated in particles of the proper size to harden the matrix.

From these considerations it was predicted that if in this instance the magnetic hardness would follow the mechanical hardness, as is generally the case for hardening produced by cold work or heat treatment of carbon-containing alloys, carbon-free dispersion hardened alloys might make useful permanent magnets.

The hardness and magnetic properties have been determined for a number of alloys after quenching from a high temperature and successive reheatings to lower temperatures, and it has been discovered that remarkable values for magnetic hardness can be obtained in carbon-free precipitation hardened alloys.[1]

Permanent magnet materials, superior to any but the cobalt magnet steels, have been developed, and these materials are all unique in that they are substantially carbon-free. As of particular interest, dispersion hardening phenomena have been disclosed in carbon-free iron-titanium alloys rich in iron.

Novel types of age hardenable ternary alloys, such as the iron-tungsten-cobalt alloys, are also described. Some of the alloys investigated reach a maximum magnetic hardness simultaneously with the maximum mechanical hardness. In other alloys the magnetic hardness attains a minimum value as the mechanical hardness reaches its maximum value.[2] This behavior is not in accord with the simpler theories of magnetism, dispersion hardening and its effect on magnetic properties, and further studies in this direction will be of material assistance in an effort to modify these theories to fit the facts more closely.

Experimental Procedure

Preparation of Alloys

Two types of furnaces were used in melting the alloys. One was a vacuum furnace of the Arsem type, having a graphite helix 4½ inches inside diameter. The pump attached to this furnace was capable of keeping the pressure at 5 or 6 millimeters of mercury during melting. The crucibles used in this furnace were made from a mixture of 90 per cent fused magnesia and 10 per cent fire clay.

[1]The work of Kroll (French Patent 669,551, February 13, 1929) in which permanent magnets were obtained by dispersion hardening of carbon-free iron-beryllium-nickel alloys was not published until after the completion of the experimental work here recorded.

[2]This failure of magnetic and mechanical hardness to coincide has been confirmed by W. Köster, *Z. Anorg. Allgem. Chem.* Vol. 179, 1929, p. 297-308.

A 35 kilovolt-ampere high frequency furnace was used in making many of the alloys. The crucibles for this furnace were from graphite, lined with an alundum-silica mixture suitably bonded.

The raw materials used were mostly of commercial grades and are given in the following list:

Iron	Electrolytic or Armco
Tungsten	Commercial Powder (98%)
Molybdenum	Powder or Commercial Carbon-Free Ferromolybdenum
Beryllium	From Beryllium Corporation of America
Titanium	Commercial Carbon-Free Ferro-alloy (20-25% Ti)
Cobalt	Shot or High Purity Electrolytic
Nickel	Electrolytic
Manganese	High Purity Carbon-Free Grade

Forging and Heat Treatment

Forgeable ingots were forged into bars ½ inch square and 12 inches long. Whenever forging difficulties were encountered, the ingots were flattened and test bars $\frac{5}{16}$ inch thick, ½ to 1 inch wide and preferably 4 inches long cut or ground from the plates.

A carbon resistor type furnace equipped with a noble metal thermocouple was used for heating the bars preparatory to quenching, which was done in water. Where the eutectic temperature was known, the alloys were quenched therefrom. When no information on the eutectic temperature was available, the alloys were quenched from a temperature below the melting point of the lowest melting composition in that series, which procedure was considered satisfactory for the purpose of this investigation.

The quenched bars were finished to the desired smoothness and "aged" at various temperatures in a muffle furnace. Each sample was tested after quenching and after each aging treatment. The bars were not, however, given a solution heat treatment after each aging treatment and consequently the effects produced at a given aging temperature are dependent in some degree on the previous agings at lower temperatures. In general, the time at aging temperature was one hour.

Testing

Hardness values were determined by means of the Rockwell hardness tester. Two permeameters were used for magnetic measurements. The longer bars were tested in the Babbitt permeameter.[3]

[3]B. J. Babbitt, "An Improved Permeameter for Testing Magnet Steel," *Journal*, Optical Society of America and *Review of Scientific Instruments*, Vol. 17, 1928, pp. 47-58.

Bars too short for the Babbitt permeameter were tested in the Fischer permeameter.[4] Bars tested in both permeameters have indicated that the two instruments give substantially the same values of remanence and coercive force.

The usual symbols, "B" for flux density in maxwells per square centimeter and "H" for field intensity in gilberts per centimeter, have been observed throughout this paper. "Bm" and "Br" are used for maximum and residual flux density, and "Hc" for coercive force. The flux density at H = 1000 gilberts per centimeter has been considered to represent the saturation value. Three observations were made at each test, namely: flux density at a field of 1000 gilberts per centimeter, remanence and coercive force. For the early part of the work on iron-tungsten alloys the maximum field intensity was 250 gilberts per centimeter.

Binary Alloys

Iron-Tungsten Alloys

According to the equilibrium diagram given by Sykes[5], an eutectic is formed in the iron-tungsten system at 48 per cent tungsten and at 1525 degrees Cent. (2775 degrees Fahr.), the components of which are an iron-rich solid solution of tungsten in iron and the compound Fe_3W_2. The solid solubility of tungsten in iron varies from 33 per cent at the eutectic temperature to 8 per cent or less at room temperature. The dispersion hardening of the iron-rich alloys results from precipitation of the compound Fe_3W_2 in a highly dispersed form from the supersaturated solid solution produced by quenching. The maximum hardness was by Sykes found to result from aging at 1290 degrees Fahr. (700 degrees Cent.).

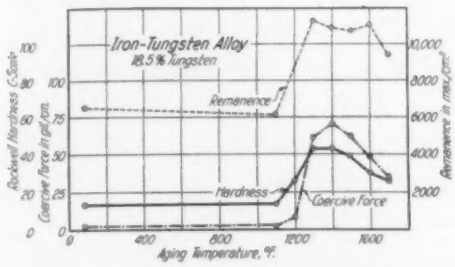
In order to determine the magnetic properties of alloys hardened by precipitation three melts, containing 18.5, 21.1 and 27.8 per cent tungsten, were prepared in the Arsem furnace. The ingots as solidified in the furnace were reheated to 2000 degrees Fahr. (1095 degrees Cent.) and forged into bars of a rectangular cross section. The forged bars were heated to 2600 degrees Fahr. (1430 degrees

[4]M. F. Fischer, "Apparatus for Determination of the Magnetic Properties of Short Bars." Scientific Papers of the Bureau of Standards, Vol. 18, 1922-1923, No. 458, pp. 513-526.

[5]W. P. Sykes, "The Iron-Tungsten System," *Transactions*, American Institute of Mining and Metallurgical Engineers, Vol. 73, 1926, pp. 968-1008.

Cent.), held at this temperature for 40 minutes and quenched in water.

The values for remanence, coercive force and hardness for the three iron-tungsten alloys are plotted against the aging temperature in Figs. 1 to 3. As these figures indicate, an increase in all three



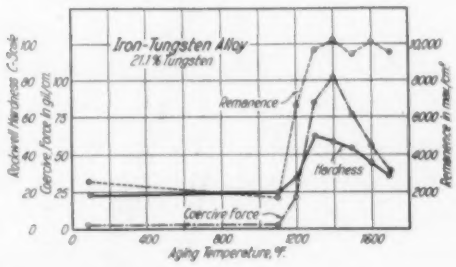


Fig. 1—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-tungsten Alloy, 18.5 per cent Tungsten.
Fig. 2—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-tungsten Alloy, 21.1 per cent Tungsten.

of these magnitudes took place in all three alloys at a temperature of 1200 degrees Fahr. (650 degrees Cent.). The marked increase in coercive force, together with the increase in hardness, demonstrates that magnetic hardness is developed as precipitation hardness occurs. The hardness appears to attain its maximum value after 5 hours aging at 1300 degrees Fahr. (705 degrees Cent.), whereas the coercive force was higher at 1400 degrees Fahr. (760 degrees Cent.)

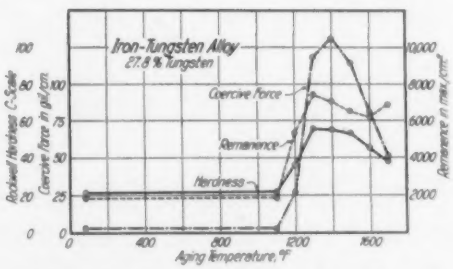


Fig. 3—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-tungsten Alloy, 27.8 per cent Tungsten.

for all three alloys. Variations in saturation values could not be followed closely on account of the change in maximum field used, but it was found that the maximum flux density after quenching, obtained with H = 250 is higher than that for H = 1000 after aging. With respect to increasing tungsten content over the range investigated, the following observations were made: Maximum hardness

increased from C43 to C57 and maximum coercive force from 70 to 151. The value of 151 was obtained for an alloy prepared in the high frequency furnace and analyzing 27.9 per cent tungsten (Table I).

The remanence decreases for increasing tungsten content, and for the highest tungsten content is only 7000 at the maximum coercive force. The coercive force together with the remanence are the chief characteristics for permanent magnets, and in the summary of data in Table I is recorded the maximum product of these two values for each alloy studied. The saturation value falls off somewhat with the tungsten content for both aged and unaged alloys.

Iron-Molybdenum Alloys

The iron-molybdenum alloys have also been carefully studied by Sykes,[6] who found that the iron-rich alloys are similar to the iron-rich tungsten alloys. The alloys are also susceptible to age hardening. In accordance with the iron-molybdenum diagram given

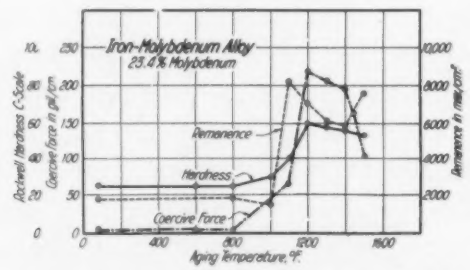


Fig. 4—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-molybdenum Alloy, 23.4 per cent Molybdenum.

in the 1930 National Metals Handbook,[7] an eutectic is formed at 36 per cent molybdenum and 1440 degrees Cent. (2625 degrees Fahr.), the components being a solid solution of molybdenum in iron and the compound Fe_3Mo_2. The solid solubility of molybdenum in iron decreases from 24 per cent at the eutectic temperature to 6 per cent at room temperature.

Only one iron-molybdenum alloy was used in this investigation. It was prepared by melting in a high purity magnesia crucible in the

[6]W. P. Sykes, "The Iron-Molybdenum System," TRANSACTIONS, American Society for Steel Treating, Vol. 10, 1926, pp. 839-870.

[7]W. P. Sykes, "Constitution of Iron-Molybdenum Alloys," *National Metals Handbook*, 1930, pp. 604-606.

Arsem furnace, and contained 23.4 per cent molybdenum. It was forged at a temperature of 2000 degrees Fahr. (1095 degrees Cent.), and quenched from a temperature of 2320 degrees Fahr. (1270 degrees Cent.). The quenching was from below the eutectic temperature, in order to prevent an undue loss of molybdenum by volatilization of molybdenum oxide.

The magnetic and hardness values plotted in Fig. 4 show that this alloy behaved in a manner similar to those of the tungsten series. The flux density at H = 1000 fell markedly as the bar began to show precipitation hardening effects due to the precipitation of the compound Fe_3Mo_2. Differing from the iron-tungsten alloys, both hardness and coercive force reached their maximum at the same aging temperature.

At the maximum coercive force, which is over 200, the remanence was only about 7000. This alloy reached the highest coercive force recorded in this investigation, namely 219. The hardness values are in agreement with those obtained by Sykes for alloys of this composition.

Iron-Beryllium Alloys

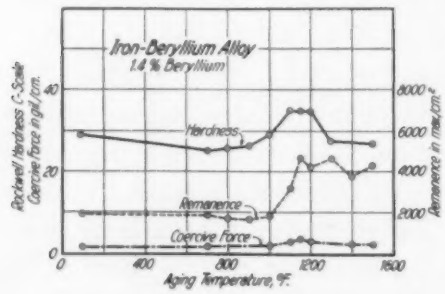
The mechanical properties of iron-beryllium alloys have been studied by Kroll,[8] who found that iron-rich alloys containing up to about 4 per cent beryllium are forgeable, and that those containing 1.2 per cent or more beryllium are susceptible to age hardening. Age hardening was developed by quenching the alloys from 1100 degrees Cent. (2010 degrees Fahr.) and aging at 520 degrees Cent. (970 degrees Fahr.). A maximum hardness of 470 Brinell was produced in the alloy containing 3.9 per cent beryllium, but the alloys were considered to be commercially valueless as they were difficult to forge and contained very large grains. The magnetic properties of these alloys were studied by Auwers,[9] who did not discover interesting magnetic properties.

For this investigation three alloys, containing 1.4, 2.9 and 5.2 per cent beryllium, were made in the high frequency furnace. The 5.2 per cent alloy could not be forged, but test specimens were prepared by grinding. The other alloys were forged at 1600 to 1800

[8]Wilhelm Kroll, "Die Legierungen des Berylliums mit Eisen." *Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern*, Vol. 8, 1929, pp. 220-235.

[9]Otto von Auwers, "Magnetische Messungen an Eisen-Berylliumlegierungen," *Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern*, Vol. 8, 1929, pp. 236-247.

degrees Fahr. (870 and 985 degrees Cent.). All alloys were quenched from 2040 to 2200 degrees Fahr. (1115 to 1205 degrees Cent.). The eutectic temperature is 2100 degrees Fahr. (1150 degrees Cent.). Microscopic examination indicated that some beryl-



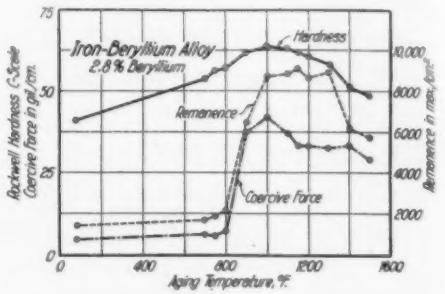
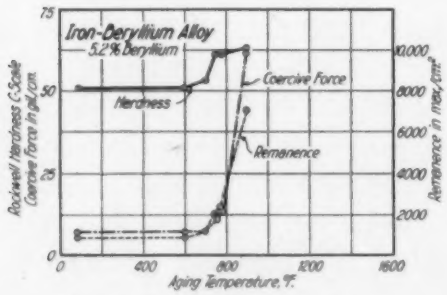


Fig. 5—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-beryllium Alloy, 1.4 per cent Beryllium.
Fig. 6—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-beryllium Alloy, 2.8 per cent Beryllium.

lium was lost from the surface during forging and heating for quenching. The 2.8 and 5.2 per cent beryllium alloys were quite brittle. The values obtained for these alloys are plotted in Figs. 5 to 8.

In contrast to the behavior of the tungsten and molybdeum alloys the saturation values as indicated by the flux density at H =



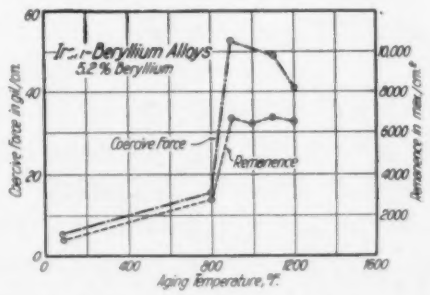


Fig. 7—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-beryllium Alloy, 5.2 per cent Beryllium.
Fig. 8—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-beryllium Alloy, 5.2 per cent Beryllium.

1000 was somewhat higher after aging than after quenching, which seems remarkable.

In the 1.4 per cent beryllium alloy the aging effect is characterized by a slight increase in hardness, coercive force and remanence at about 1100 degrees Fahr. (595 degrees Cent.). Figs. 9 to 12 show the microstructures of the 2.8 and 5.2 per cent alloys in the quenched and in the aged conditions. The large polyhedral grains

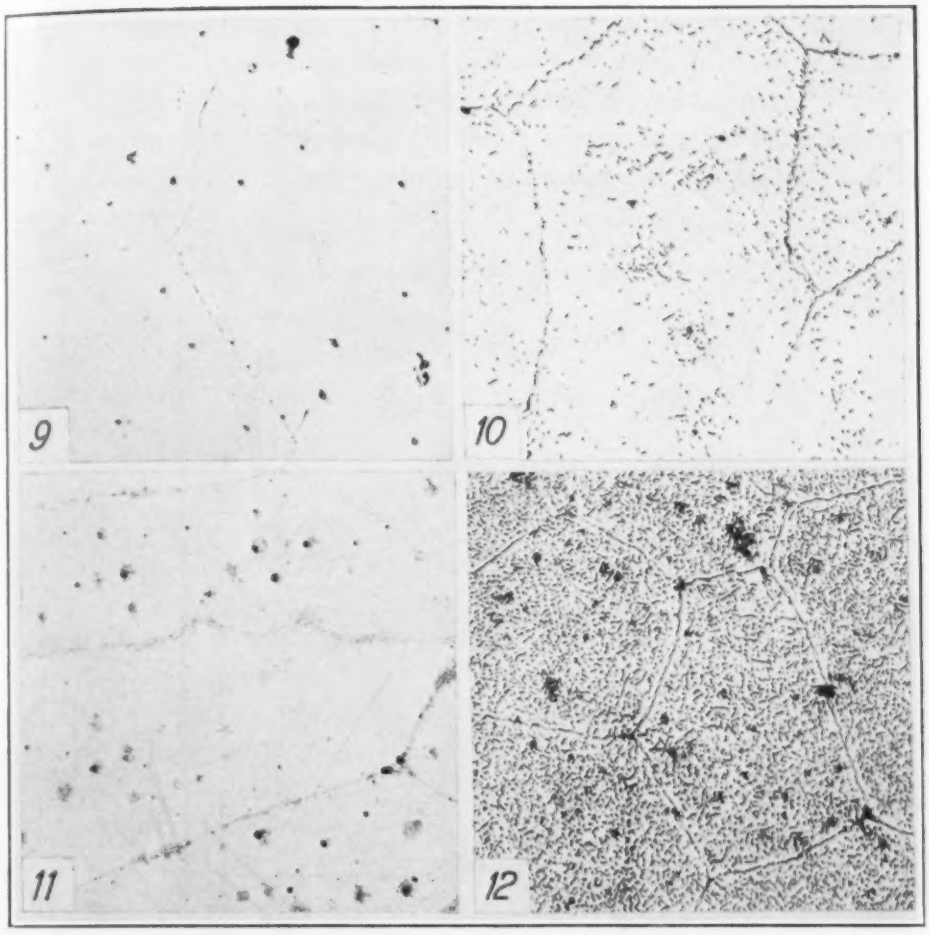


Fig. 9—Iron-beryllium Alloy (2.8 per cent Beryllium) As-quenched from 2200 Degrees Fahr. × 300
Fig. 10—Iron-beryllium Alloy (2.8 per cent Beryllium) After Aging at 1700 Degrees Fahr. × 300
Fig. 11—Iron-beryllium Alloy (5.2 per cent Beryllium) As-quenched from 2040 Degrees Fahr. × 300
Fig. 12—Iron-beryllium Alloy (5.2 per cent Beryllium) After Aging at 1700 Degrees Fahr. × 300

and the precipitated compound in the aged state is evident. Fig. 10 indicates that the solubility of beryllium in iron at low temperatures is less than 2.8 per cent.

Iron-Titanium Alloys

Lamort[10] has investigated the equilibrium diagram for alloys containing up to 22 per cent titanium, which composition corresponds very closely to the nonmagnetic compound Fe_3Ti. The iron-

[10] J. Lamort, "Ueber Titaneisenlegierungen," *Mitteilungen aus dem Eisenhüttenmännischen Institut der königl. techn. Hochschule Aachen*, Vol. 6, 1915, pp. 175-185.

titanium diagram in Fig. 13, as given by Lamort, shows that the melting point of iron is lowered on addition of titanium up to the eutectic composition of 13.2 per cent titanium.

Lamort reports a solid solubility of 6 per cent titanium in iron, and according to his solubility curve in Fig. 13 the solubility does not vary with temperature. However, a critical survey of the rela-

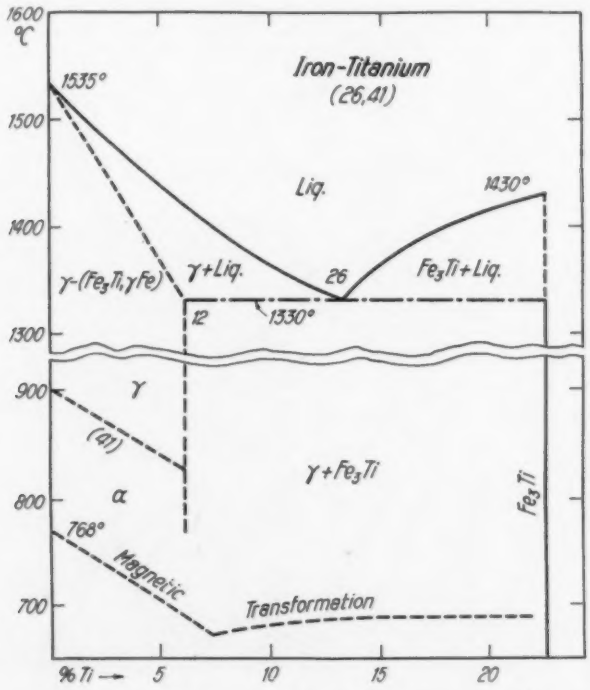


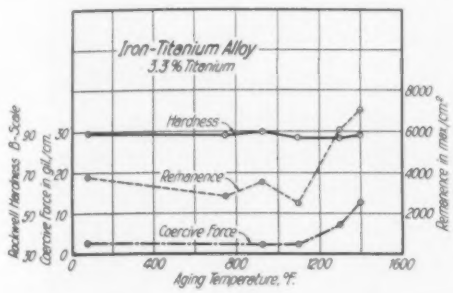
Fig. 13—Iron-titanium Diagram. (Reproduced from International Critical Tables, 1927, 2.453.)

tively meager data available on these alloys gave promise that age hardenable properties might be disclosed.

A series of alloys containing up to 7 per cent titanium was prepared by adding ferrotitanium to molten iron in a high frequency induction furnace. The alloys contained the following quantities of titanium: 0.5, 2.9, 3.3, 4.0, 4.9, 5.4 and 7.1 per cent. The ferrotitanium used contained 20 to 25 per cent titanium and substantial amounts of aluminum and silicon. The ingots were forged at 1800 to 1900 degrees Fahr. (980 to 1040 degrees Cent.), and the rods quenched in water from the eutectic temperature of 2370 degrees Fahr. (1300 degrees Cent.).

The samples were heat treated and tested in the manner previously described for the other alloys. The values at maximum co-

ercive force for the seven alloys are included in Table I. Age hardening properties were first observed in the alloy containing 3.3 per cent titanium. The hardness and magnetic values for this alloy are shown in Fig. 14. Fig. 15 gives similar values for the alloy contain-



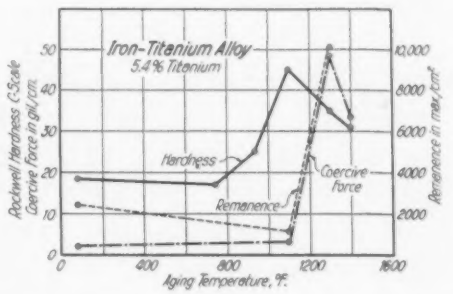
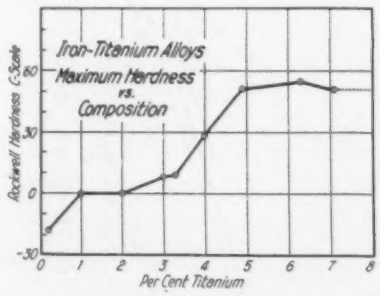


Fig. 14—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-titanium Alloy, 3.3 per cent Titanium.
Fig. 15—Change of Rockwell Hardness, Coercive Force and Remanence With Aging Temperature of Iron-titanium Alloy, 5.4 per cent Titanium.

ing 5.4 per cent titanium. The behavior of this alloy is typical of the alloys containing over 4 per cent titanium.

The maximum Rockwell hardness of this series of alloys as a function of the titanium content is shown in Fig. 16. Fig. 17 shows the maximum coercive force values obtained. Judged by these two



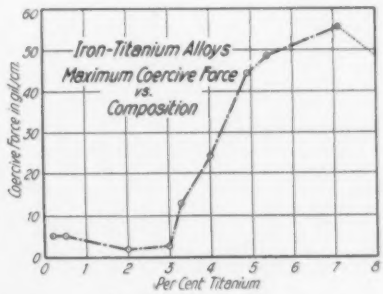


Fig. 16—Maximum Rockwell Hardness of Heat Treated Iron-titanium Alloys as a Function of the Titanium Content.
Fig. 17—Maximum Coercive Force of Heat Treated Iron-titanium Alloys at a Function of the Titanium Content.

curves the solubility of titanium in iron is approximately 6 per cent at the eutectic temperature and 3 per cent or less at room temperatures.

In the alloys that were susceptible to age hardening the hardening began at about 750 degrees Fahr. (400 degrees Cent.) and the maximum hardness was found after heating to 1100 degrees Fahr. (595 degrees Cent.). At temperatures above 1100 degrees Fahr.

(595 degrees Cent.) the hardness decreased. The coercive force of the quenched alloys was around 2 to 5 gilberts per centimeter, and remains unchanged at an aging temperature of 1100 degrees Fahr. (595 degrees Cent.), at which temperature the maximum hardness was developed.

At an aging temperature of 1300 degrees Fahr. (705 degrees Cent.) the coercive force of the age hardenable alloys is suddenly increased. The temperature of the maximum magnetic hardness does not, then, correspond to the temperature of maximum mechanical hardness, and apparently the precipitated iron-titanium compound must have a particle size larger than that of critical dispersion for maximum strengthening in order to produce magnetic hardness.

In general the saturation value decreases with increasing titanium content. The remanence increases as the coercive force increases. It was found that direct aging at 1300 degrees Fahr. (705 degrees Cent.), omitting the 1100 degrees Fahr. (595 degrees Cent.) aging, produced the higher remanence, whereas aging at 1100 degrees Fahr. (595 degrees Cent.) previous to aging at the higher temperature gave the higher coercive force.

The photomicrographs shown in Figs. 18 and 19 substantiate the hardness and magnetic properties in showing that the solubility of titanium decreases with decreasing temperature.

Properties of Binary Alloys

Some of the data on binary alloys are summarized in Table I, which gives the values for each alloy in the quenched condition, the maximum hardness produced by aging, the maximum remanence and coercive force produced by aging, and other magnetic values associated with the maximum value of coercive force. The product of coercive force by remanence (Hc x Br) is used by some investigators as a merit index for permanent magnet steels, and is given here not because the authors regard it as a true index of quality, but merely to enable convenient comparison of our results with values published for the magnet steels now used.

The data given in Table I prove that the increase in coercive force, or magnetic hardness, on aging is at least as striking as the increase in mechanical hardness. Although the values of remanence are slightly lower, the coercive force values of some of these aged alloys are higher than are found in any but cobalt magnet steels.

Table I

Hardness and Magnetic Values of Binary Alloys

Values for Aged Alloys Represent Maximum Hardness, Maximum Remanence, Maximum Coercive Force and Other Magnetic Values Associated with the Maximum Coercive Force.*

Alloy Per Cent	Condition	Rockwell Hardness	Remanence	Magnetic Values Associated with Maximum Coercive Force: Coercive Force Hc	Saturation Bm at H = 1000	Remanence Br	Hc x Br x 10^{-6}
18.5 W	Quenched	C13	6,550	1.8	17,080**		
	Aged	C43	11,320	70.0	16,120	10,900	0.763
21.1 W	Quenched	C18	3,340	1.8	17,920**		
	Aged	C48	9,940	85.0	15,050	9,070	0.770
21.1 W	Quenched	C19	2,570	2.5	17,440**		
	Aged	C50	10,250	102.5	15,130	8,640	0.885
27.8 W	Quenched	C21	1,990	3.0	16,350**		
	Aged	C55	7,400	130.0	14,620	6,980	0.907
27.9 W	Aged	C57	6,790	151.0	12,340	6,790	1.020
23.4 Mo	Quenched	C25	1,760	2.5	16,750		
	Aged	C60	8,280	219.	10,600	7,000	1.533
	Aged	C59	8,980	207.5	10,320	6,270	1.301
1.4 Be	Quenched	C29	1,900	1.5	20,100		
	Aged	C35	4,640	3.5	20,150	4,640	0.016
2.8 Be	Quenched	C41	1,400	4.7	13,500		
	Aged	C64	9,100	42	15,150	8,700	0.365
5.2 Be	Quenched	C51	840	7.2	12,100		
	Aged	C63	7,030	62.5	13,000	7,030	0.440
5.2 Be	Quenched	...	890	5.0	11,380		
	Aged	...	6,710	52.5	12,700	6,450	0.338
0.5 Ti	Quenched	B84	7,380	4.8	20,330		
	Aged	B87	9,360	5.0	20,650	6,750	0.034
2.94 Ti	Quenched	B85	1,180	2.1	18,700		
	Aged	B89	4,860	2.7	18,600	3,780	0.011
3.3 Ti	Quenched	B89	3,800	2.5	19,300		
	Aged	B90	7,060	12.8	18,150	7,060	0.090
4.0 Ti	Quenched	C14	2,600	2.3	17,650		
	Aged	C28	9,500	24.4	15,000	9,140	0.223
4.9 Ti	Quenched	C19.5	2,540	3.5	15,580		
	Aged	C51	8,660	44.5	14,520	8,660	0.385
5.4 Ti	Quenched	C19	2,400	2.3	17,450		
	Aged	C45***	10,100	48.6	14,900	8,330	0.405
7.1 Ti	Quenched	C24	960	3.5	17,900	960	
	Aged	C51	7,970	55.5	14,300	7,250	0.401

*The maximum values for hardness, remanence and coercive force are given in the figures.

**H max. = 250.

***A maximum hardness of C45 is shown in Fig. 15. Evidently the optimum hardness value was not developed in this particular bar.

Complex Alloys

Several ternary and quaternary alloys were studied, and the results will be briefly summarized.

Iron-Tungsten-Cobalt Alloys

These alloys were made for the purpose of investigating age hardening effects in alloys consisting of tungsten in the iron-cobalt combination 65 iron and 35 cobalt, which is known to have a remarkably high saturation value.

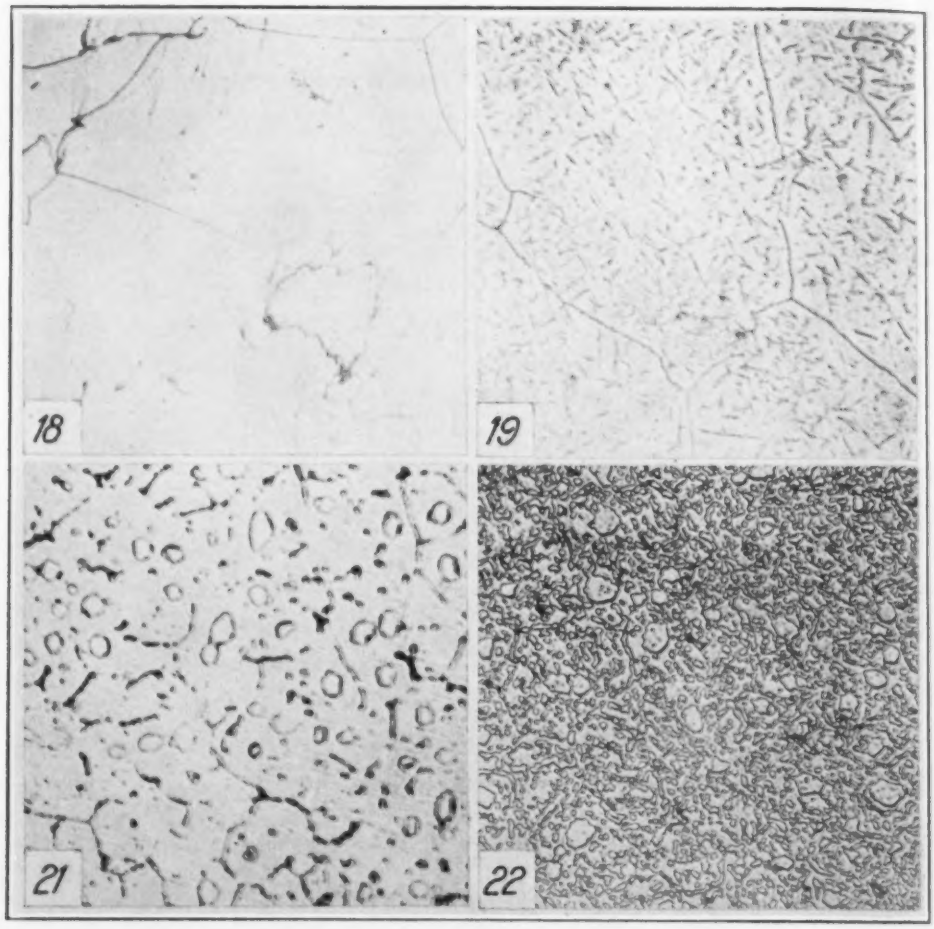


Fig. 18—Iron-titanium Alloy (5.4 per cent Titanium) As-quenched from 2370 Degrees Fahr. × 100
Fig. 19—Iron-titanium Alloy (5.4 per cent Titanium) As-Forged. × 100
Fig. 21—Iron-cobalt-tungsten Alloy (27.7 per cent Tungsten, 24 per cent Cobalt) As-quenched from 2600 Degrees Fahr. × 600
Fig. 22—Iron-cobalt-tungsten Alloy (27.7 per cent Tungsten, 24 per cent Cobalt) After Extended Aging at 1950 Degrees Fahr. × 600

Two alloys, one containing 27.7 per cent tungsten, the other 21.1 per cent tungsten, balance iron and cobalt in the ratio mentioned above, were prepared in the Arsem furnace. The ingots were difficult to forge, but could be flattened to a blank, from which test bars were ground. The bars were quenched from 2600 degrees Fahr. (1430 degrees Cent.).

The values obtained for the bars as quenched and after aging are summarized in Table II, and the values obtained for the 27.7 per cent tungsten alloy are plotted in Fig. 20. Both alloys exhibit age hardening effects, the one with the higher tungsten content

reaching a hardness of C67 upon aging at 1100 degrees Fahr. (595 degrees Cent.).

The coercive force of these alloys displays a rather remarkable behavior, as it decreases after reaching a temperature of 800 degrees Fahr. (425 degrees Cent.), and is at a minimum as the hardness attains its maximum, analogous to the phenomena observed in binary iron-titanium alloys. For further increase in aging temperature the

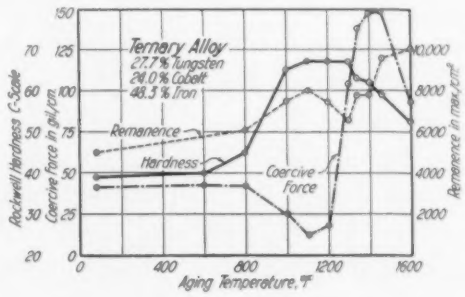


Fig. 20—Change of Rockwell Hardness, Coercive Force and Remanence with Aging Temperature of Iron-cobalt-tungsten Alloy (27.7 per cent Tungsten, 24 per cent Cobalt.)

coercive force rises rapidly. For the alloy of higher tungsten content a maximum coercive force of 150, or the same as observed for the binary alloy, is found, but due to the presence of cobalt the value for remanence is considerably higher, namely, 9600 as compared with 7000 for the binary alloy.

Photomicrographs of the 27.7 per cent tungsten alloy are shown in Figs. 21 and 22. A number of kernel-like areas appearing in the quenched alloy, Fig. 21, indicates that complete solid solubility does not exist. Fig. 22 shows the alloy after an extended aging at 1950 degrees Fahr. (1065 degrees Cent.), the structure resembling that of a carbon tool steel with spheroidized cementite.

A number of alloys of varying tungsten and cobalt content were melted in air in the high frequency furnace. These alloys as cast in chilled molds can be aged directly, omitting the quenching operation. By this method could be produced tools for cutting hard rubber, and very promising performances were obtained from such tools.

Iron-Tungsten-Nickel Alloys

Several alloys of this type were made in an attempt to substitute nickel for cobalt. It was believed that even if magnetic properties

Table II

Hardness and Magnetic Values of Complex Alloys

Values for Aged Alloys Represent Maximum Hardness, Maximum Remanence, Maximum Coercive Force and Other Magnetic Values Associated with this Coercive Force.

Alloy Per Cent	Condition	Rockwell Hardness	Remanence	Magnetic Values Associated with Maximum Coercive Force			
				Coercive Force Hc	Saturation Bm at H = 1000	Remanence Br	Hc x Br x 10^{-6}
27.7 W	Quenched	C39	5,000	42.0	15,700		
24.0 Co	Aged	C67	10,000	148.6	16,500	9,600	1.426
22.1 W	Quenched	C33	6,320	38.6	17,380		
26.5 Co	Aged	C63	10,850	106.2	14,460	8,070	0.858
19.2 Mo	Quenched	C43	4,340	62.7	12,750		
23.3 Co	Aged	C66	7,010	128.0	12,900	6,050	0.775
20.0 W	Quenched	C35	5,310	36.6	16,930		
6.0 Mn							
26.0 Co	Aged	C63	8,560	150.0	13,600	6,550	0.980

were low, interesting hardness characteristics might be obtained. The results were, however, disappointing insofar as the alloys did not display age hardening properties.

Iron-Molybdenum-Cobalt Alloys

The same proportion of iron and cobalt mentioned above was used in an alloy containing molybdenum. The intended composition was 24 per cent of molybdenum and 26.5 per cent of cobalt, but analysis indicated only 19.3 per cent molybdenum and 23.3 per cent cobalt.

Difficulty was experienced in the forging operation and only one test bar could be made from this melt. The results for the as quenched and aged bar are shown in Table II. As will be seen, the alloy is similar in its properties to the corresponding tungsten alloy, except for the lower saturation flux density, which may be partly accounted for by the unsoundness of the bar.

Ternary Iron-Titanium Alloys

A few ternary iron-titanium alloys were prepared. Addition of chromium or manganese in amounts of 3 to 4 per cent show little of interest in magnetic respect. The coercive force increases somewhat by the addition of tungsten, but at the same time a decrease in remanence takes place. An iron-titanium-cobalt alloy was found to retain its hardness at elevated temperatures to a remarkable extent.

One iron-titanium-carbon alloy, analyzing 4.4 per cent titanium

and 0.69 per cent carbon, was also made. The maximum hardness obtained in this alloy by any heat treatment was C27, indicating that at this composition we are entirely in the alpha range.

Other Types of Alloys

Several types of quaternary alloys have been more or less sporadically investigated. Only one type of such alloys will be described, namely, the iron-tungsten-cobalt-manganese alloys. Ternary alloys of iron-tungsten-cobalt as mentioned above are practically unforgeable. By adding a small percentage of manganese, these alloys are rendered forgeable. Forgeable alloys of this class can be produced which will give a Rockwell C hardness of around 70, and may find application for special type of tools.

Some of the values obtained for an alloy containing 20 per cent tungsten, 6 per cent manganese and the balance iron and cobalt in the ratio 65 to 35 are listed in Table II. It appears that whereas manganese in the amount added tends to give less marked minimum in the coercive force curve, the maximum value is higher than for a corresponding manganese free alloy. Saturation and remanence are, however, lowered by the addition of manganese.

Discussion

For only three of the numerous alloys described in the preceding do we know the composition of the precipitated compounds, namely, for the binary iron-tungsten alloys (Fe_3W_2), iron-molybdenum alloys (Fe_3Mo_2) and iron-titanium alloys (Fe_3Ti).

Assuming that the precipitation of an intermetallic compound produces a coercive force, an attempt has been made in the following to correlate the coercive force obtained in dispersion hardened binary alloys with content of age-hardening element and the composition of the precipitated compound.

It appears that the maximum coercive force in an age-hardened binary alloy, the composition of which is within the range of maximum solid solubility, is proportional to the "effective" percentage of the alloying element, by which is meant the actual percentage diminished by the room temperature solubility. This principle will be applied to the iron-tungsten alloys.

Iron-Tungsten Alloys

The room temperature solubility of tungsten in iron is 8 per cent, and we have them according to the results obtained in this paper.

Alloy No.	Per Cent Tungsten	"Effective" Percentage	Max. Coercive Force Obtained
1	18.5	10.5	70.0
2	21.1	13.1	102.5
3	27.9	19.9	151.0

Assuming the coercive force to be proportional to the "effective percentage," the coercive forces of alloys No. 1 and 2 are calculated below, based on the value obtained for alloy No. 3 (See Table I).

Alloy No. 1:

$$Hc = 151 \times \frac{10.5}{19.9} = 79.7 \text{ (observed value} = 70)$$

Alloy No. 2:

$$Hc = 151 \times \frac{13.1}{19.9} = 99.5 \text{ (observed value} = 102.5)$$

The calculated and observed values agree within the expected accuracy, and this method evidently offers a means of following the aging procedure in these alloys.

Whereas for one type of alloy, such as the iron-tungsten alloys, the coercive force is proportional to the effective percentage of the alloying element (tungsten) or precipitated compound (Fe_3W_2), it appears that the coercive force in binary alloys is determined by the ratio of the "effective percentage" of the age-hardening element to the molecular weight of the precipitated compound, provided, of course, that the compound is precipitated in a form that produces a coercive force.

We will briefly illustrate the consequence of this conception for iron-molybdenum and iron-titanium alloys.

Iron-Molybdenum Alloy

The room temperature solubility of molybdenum in iron is 6 per cent. For the alloy reported in Table I we have:

Per Cent Molybdenum	Effective Percentage	Max. Coercive Force Obtained
23.4	17.4	219
Molecular weight of the compound Fe_3W_2:		535.4
Molecular weight of the compound Fe_3Mo_2:		359.4

Based on the value of Hc = 151 observed for iron-tungsten alloy No. 3, we find by applying the rule given above:

$$\text{Hc} = 151 \times \frac{17.4}{19.9} \times \frac{535.4}{359.4} = \underline{197} \text{ (observed value} = 219)$$

Iron-Titanium Alloy

From the results obtained in this investigation, it appears that the room temperature solubility of titanium in iron is around 3 per cent, and that the maximum of solid solubility may be roughly estimated at 6 per cent in agreement with the findings of Lamort.

The maximum effective percentage in iron-titanium alloys will, therefore, be around 3 per cent.

The molecular weight of the compound Fe_3Ti = 215.4.

By calculating as described under iron-molybdenum alloy we find:

$$\underset{\text{Max.}}{\text{Hc}} = 151 \times \frac{3.0}{19.9} \times \frac{535.4}{215.4} = \underline{56.4} \text{ (observed max.} = 50 - 55).$$

These calculations are as yet only speculative, and sufficient data are not at hand to definitely prove or disprove the validity of the conceptions set forth.

Conclusions

1. The relation of magnetic properties to physical hardness has been investigated for quite a number of age-hardenable alloys, and the fact has been established that permanent magnets can be produced by age-hardening of carbon-free iron alloys.

2. A binary iron-tungsten alloy shows a good combination of coercive force and remanence.

3. A binary iron-molybdenum alloy exhibits the highest coercive force of the alloys investigated.

4. An iron-beryllium alloy attained the greatest hardness of the binary alloys.

5. Binary iron-titanium alloys display age-hardening properties and in magnetic respect behave in a rather irregular manner.

6. Quite a number of ternary and quaternary age-hardenable alloys have been investigated. Ternary alloys of iron-tungsten-cobalt

and iron-molybdenum-cobalt show unusual age-hardening properties. Iron-tungsten-cobalt alloys exhibit the best magnetic characteristics of any of the alloys investigated and are superior to any other permanent magnet material with the exception of cobalt magnet steel.

7. In general all of the alloys which show age-hardening properties exhibit a change in coercive force and remanence upon aging. This phenomenon is evidently typical for these alloys. An increase in coercive force is, however, by no means coincident with the increase in hardness, and the two properties may within certain temperature ranges undergo changes in opposite directions. In view of this, present conceptions concerning the relation of coercive force to physical hardness of permanent magnets will need modification. The results arrived at show that permanent magnets possessing promising characteristics may be produced from carbon-free age-hardenable iron alloys, which offer an interesting field for further explorations.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to R. S. Dean, now of the U. S. Bureau of Mines, and to J. L. Gregg, now of the Battelle Memorial Institute, for their initiation and direction of this work while members of the Western Electric Company's Metallurgical Staff and also for valuable assistance from them in the preparation of the paper.

DISCUSSION

Written Discussion: By W. P. Sykes, metallurgical engineer, Incandescent Lamp Department, General Electric Company, Cleveland.

The authors have made a valuable contribution to our knowledge of physical metallurgy. It is from such data as this that we may hope to arrive at a more complete understanding of the physical laws governing the structure of metals and alloys.

I should like to call attention to one or two points which may have some significance in connection with the hardening of the binary alloys described in this paper. The micrographs indicate that the iron-rich solid solutions of beryllium and titanium are both relatively coarse-grained in the quenched state. From this we may conclude that these compositions lie within the field of the body-centered cubic lattice and that no transformation occurs during cooling in the iron-rich solid solutions.

In this respect then these alloys are similar to the iron-rich solid solutions in the iron-tungsten and iron-molybdenum systems.

Moreover the iron-beryllium alloys develop a secondary hardness of the same magnitude as the above mentioned alloys (Rockwell C55 to C65).

Strictly speaking, the increase in hardness brought about by aging should bear a close relationship to the quantity of the precipitated phase, but for purposes of an approximate comparison we may consider the total amount of the second element present in these alloys in the range of composition which develops the maximum hardness. Now 3 per cent by weight of beryllium in iron represents about 16 atomic per cent. The comparable hardness values in the iron-tungsten and iron-molybdenum alloys likewise occur in the range of 15 to 18 atomic per cent tungsten and molybdenum.

On the other hand note that the maximum hardness of Rockwell C51 in the iron-titanium series occurs in the alloy containing some 6 per cent by weight titanium. This represents but about 7 atomic per cent. A comparison of the atomic volumes of these four alloying elements shows titanium with 10.7 to be somewhat larger than tungsten (9.5) and molybdenum (9.3) while beryllium has the much smaller atomic volume of 4.9.

The foregoing points have been cited merely as examples of some of the many factors which obviously must be considered in any fundamental study of precipitation hardening or "age hardening."

The ternary alloys of iron-tungsten-cobalt described by the authors are perhaps the most remarkable of all on account of their unusual age-hardening properties as well as their magnetic characteristics.

Some time ago while exploring the field of modified iron-tungsten alloys I likewise observed the striking changes brought about by replacing part of the iron with cobalt. The most important effects of such substitution appear

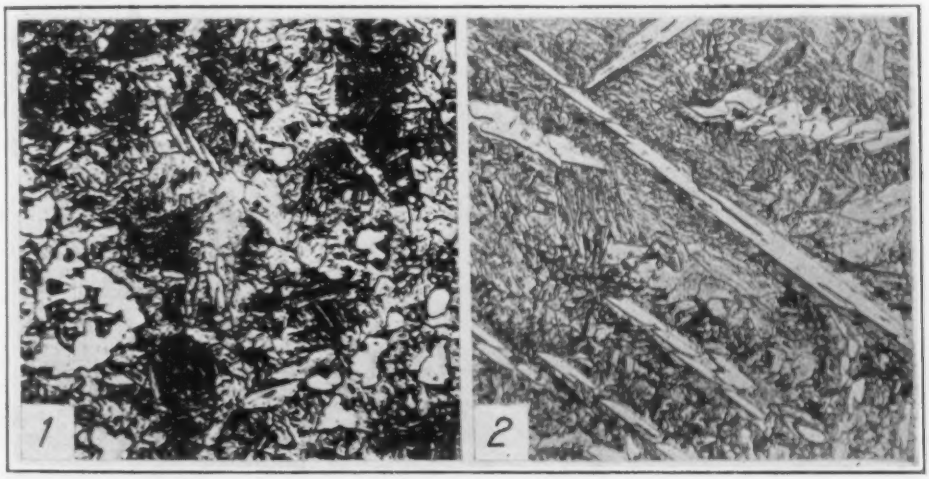


Fig. 1—Alloy Containing 30 per cent Tungsten, 25 per cent Cobalt and 45 per cent Iron. Pressed Powders, Sintered at 1450 degrees Cent. (2640 degrees Fahr.) 2 Hours. Quenched from 1450 degrees Cent. × 300

Fig. 2—Alloy containing 30 per cent Tungsten, 25 per cent Cobalt and 45 per cent Iron. Alloy Formed by Melting. Quenched from 1450 degrees Cent. (2640 degrees Fahr. × 300

to be (1), an increase in the primary hardness, i.e., hardness in the quenched condition. (2) A lowering of the minimum temperature at which age-hardening occurs. (3) A considerable increase in the maximum secondary hardness.

As an example let me describe the performance of an alloy made up of 30

per cent tungsten, 25 per cent cobalt and 45 per cent iron. This alloy as formed by pressing the mixed powders, sintering at about 1450 degrees Cent. (2640 degrees Fahr.) in a hydrogen atmosphere and quenching from this temperature showed a Rockwell hardness of C38. After aging at 500 degrees Cent. (930 degrees Fahr.) for one hour the hardness had increased to C64. At the end of 10 hours the hardness measured C68 and after 100 hours at 500 degrees Cent. (930 degrees Fahr.) the alloy had developed a hardness of Rockwell C70.

This same hardness value of C70 is obtained by aging at 600 degrees Cent. (1110 degrees Fahr.) for one hour. It is interesting to observe in addition, that this hardness has not decreased more than one point (to C69) after 25 hours at 600 degrees Cent. This fact indicates a considerable stability at elevated temperatures.

In the microstructure of an alloy such as I have described, we find that in the quenched state the iron-rich ground mass has what might be called a martensitic structure. This is doubtless the result of the presence of cobalt which tends to keep the iron in the face-centered cubic form at the quenching temperature even in the presence of 30 per cent by weight of tungsten. In this instance, then, we have initially a "fine-grained" ground mass or solid solution upon which to superimpose the additional precipitation hardening produced by subsequent aging. This is a vastly different state of affairs than that which exists in the binary iron-tungsten and iron-molybdenum alloys in which the solid solution is always extremely coarse-grained due to the absence of any transformation during the quench.

The accompanying microphotographs illustrate the acicular structure of the solid solution in such an alloy as quenched. In one case the alloy has been formed in the solid by the sintering process and in the second case the alloy was made by melting.

Authors' Closure

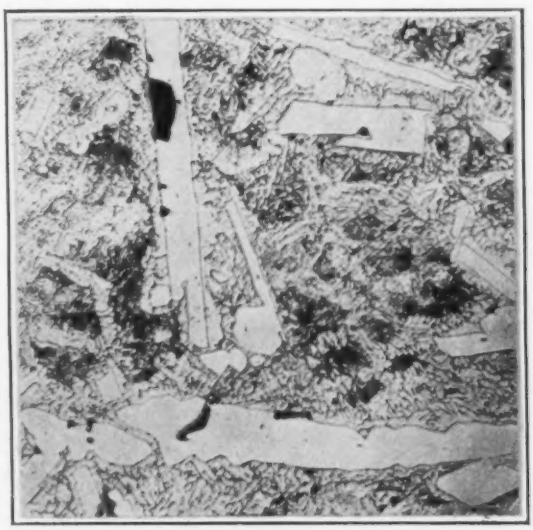
The authors wish to thank Mr. Sykes for his carefully prepared and interesting discussion. He touches on several points which are of great importance in connection with the present paper and to which the authors have given considerable thought.

The iron-rich solid solutions of iron-beryllium and iron-titanium alloys are both relatively coarse-grained in the quenched condition. The large grain size and the inherent brittleness of heat treated carbon free iron-titanium alloys constitute the main objections to their practical application. Two iron-titanium melts, analyzing 4.9 and 5.5 per cent titanium respectively, were made on a semi-commercial scale and cast into ingots approximately six inches square, weighing around 100 pounds each. The ingots could be readily forged to the desired dimensions, using quite heavy reductions. However, test bars quenched after various periods of heating at the temperature required to bring the iron titanide into solution, all possessed a coarse grain structure, and considerable difficulty was experienced in the various machining operations performed on a quenched test block.

An attempt was made to refine the grain structure by the addition of elements such as chromium, cobalt and manganese. Manganese appeared to act

as a grain refiner, but the practicability of producing ternary age hardenable iron-titanium alloys with a refined structure was not investigated in detail. R. Wasmuht[1] in a recent article states that age hardened iron-titanium alloys containing silicon may be refined without reducing the precipitation hardness by the addition of manganese, nickel or chromium.

Mr. Sykes brings out in his discussion that it may be concluded, based on the coarse-grained structure in the quenched condition, that no transformation occurs in the iron-rich solid solutions of beryllium and titanium during cooling. No doubt the transformations indicated in the iron-beryllium and the iron-titanium diagrams (See International Critical Tables, Vol. 2, 1927, p. 451, and Fig. 13 of this paper) will need revision. An article by Wever[2] has



Alloy of Iron-Cobalt and Tungsten as Cast. The Intended Composition was 30 per cent Tungsten, 24.5 per cent Cobalt and 45.5 per cent Iron. × 500

recently come to our attention. He gives a closed gamma region for iron-beryllium alloys, and the limit of the existence of the gamma phase as approximately 0.4 per cent beryllium. A further study of transformations in iron-titanium alloys should also be of considerable interest in connection with the observed anomalous magnetic behavior.

The exact solid solubility-temperature curve as well as transformations should preferably be determined in alloys of higher purity than the ones used for the present investigation. Our source of ferrotitanium contained substantial amounts of aluminum and silicon. The absence of transformations in the iron-rich solid solutions of binary iron-tungsten, iron-molybdenum, iron-beryllium and iron-titanium alloys would simplify the classification of such alloys.

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[1]R. Wasmuht, "Die Ausscheidungshärtung des Eisens durch Titan," *Archiv für das Eisenhüttenwesen*, Vol. 5, 1931-32, p. 45-56.

[2]F. Wever, Über Eisen-Beryllium- und Eisen-Bor-Legierungen und die Struktur des Eisenborides," *Zeitschrift für Technische Physik*, Vol. 10, 1929, p. 137-138.

The question of the relationships which may or may not exist between the properties of the aged alloys and the quantity and nature of the precipitated compound is a very difficult one. In the present paper an attempt has been made to correlate the coercive force with the "effective percentage" of the added element and the molecular weight of the precipitated compound. Although the authors consider their tentative calculations to be of little actual value, it is hoped that some investigator may find this phase of the subject to be of interest after further data have been collected. If a relationship does exist, it should, in our opinion, be based mainly on the quantity of the precipitated phase, and probably the relative volumes occupied by the precipitated compound and the iron-rich ground mass will play an important part.

Mr. Sykes has also studied iron-tungsten-cobalt alloys of the composition described in this paper, and his data are in good agreement with those reported by the authors. We note with great interest his explanation of the microstructure of quenched iron-cobalt-tungsten alloys as due to the presence of a transformation during quenching. Our Fig. 21 represents a forged alloy containing 27.7 per cent tungsten, 24 per cent cobalt, and balance iron, after quenching from 2600 degrees Fahr. (1425 degrees Cent.). The accompanying photomicrograph shows the microstructure of another alloy of intended composition 30 per cent tungsten, 24.5 per cent cobalt and balance iron, as cast in a chilled mold at a rapid rate of cooling. The acicular structure of this alloy resembles that of an alloy of corresponding composition given by Mr. Sykes in Fig. 2 as alloy formed by melting and quenched from 1450 degrees Cent. (2640 degrees Fahr.).

ALLOYS OF IRON, MANGANESE AND CARBON—Part I

Preparation of Alloys

By Francis M. Walters, Jr.

Abstract

Despite the importance of manganese as an alloying element, comparatively little systematic investigation has been made of the iron-manganese-carbon system.

The materials used in the preparation of the alloys were distilled manganese and electrolytic iron melted in vacuo.

The alloys were melted in an induction furnace under argon at atmospheric pressure, because of the high vapor pressure of manganese. Commercial argon was purified by passing over red-hot metallic calcium and copper oxide, and through absorbents for water and carbon dioxide. The melts were allowed to freeze in the furnace.

The crucibles were of c.p. magnesium oxide and were fired in an induction furnace.

The melts, if not overheated, lost little manganese. Over twenty melts with carbon 0.02 per cent or less have been made for 0 to 100 per cent manganese, and about twenty more have been made with various percentages of carbon up to 1.65 per cent.

Introduction

THE importance of manganese as an alloying element with iron is generally recognized. The relative cheapness of manganese and the remarkable properties which it confers upon iron make it seem strange that its practical applications should be limited to low percentages and to steels of the Hadfield type. The interest in manganese is even greater from the scientific point of view than from the practical. Until a few years ago, manganese and iron were

The work here described is in cooperation with the Iron Alloys Committee of the Engineering Foundation, whose support is gratefully acknowledged. Acknowledgment is made to those who kindly read the manuscripts which have been approved for publication by the Metallurgical Advisory Board.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, Francis M. Walters, Jr., is a member of the society and is director of the Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 9, 1931.

generally supposed to form a "continuous series of solid solutions," but the work of Wohrman[1] and the work of various investigators[2] in the field of X-rays have shown that the alloys of iron and manganese are far from simple.

Relatively little work has been done on the iron-manganese-carbon system. A large part of the work that has been carried out has been from the practical standpoint, and the purity of the alloys studied has been only that which might reasonably be obtained in commercial practice.[3] The most important investigation in which an attempt was made to prepare really pure alloys of iron, manganese, and carbon, was that carried out at the Bureau of Standards.[4] In this investigation, however, the maximum manganese content was 2 per cent. It is not surprising that more work has not been done on the preparation of pure iron-manganese alloys when the difficulties experienced in the purification of manganese are understood. Methods successfully applied to other elements proved tedious or impossible in the case of manganese. It was not until the application of the high frequency induction furnace that the method of distillation[5] became practical for the preparation of pure manganese for an extensive experimental program.

It is unfortunate that the study of the various properties of alloys has been carried out by as many different workers as there have been properties studied. One man has studied the mechanical properties of a given series of alloys, another has determined the electrical characteristics of the same alloy but on a different series of melts, while still another has studied the magnetic properties; so that, when any attempt is made to correlate the data, surprising discrepancies

[1]C. R. Wohrman, "Heterogeneity of Iron-Manganese Alloys," Technical Publication No. 14, American Institute of Mining and Metallurgical Engineers, 1927.

[2]E. C. Bain, "Nature of Solid Solutions," *Chemical and Metallurgical Engineering*, Vol. 28, No. 1, 1923, p. 21.
Winfried Schmidt, "X-ray Investigations of the Iron-Manganese System," *Archiv für das Eisenhüttenwesen*, Vol. 3, October 1929, p. 293.
Einar Öhman, "X-ray Investigations of the Iron-Manganese System," *Zeitschrift für Physikalische Chemie*, Abt. B, Vol. 8, June 1930, p. 81.

[3]Sir Robert Hadfield, "Alloys of Iron and Manganese Containing Low Carbon," *Journal*, Iron and Steel Institute, Vol. 115, 1927, p. 297.

[4]Robert P. Neville and John R. Cain, "Effects of Carbon and Pure Manganese on the Mechanical Properties of Pure Iron," Bureau of Standards, Scientific Papers, No. 464, Vol. 18, 1923, p. 411.
Henry S. Rawdon and Frederick Sillers, "Effect of Manganese on the Structure of Alloys of the Iron-Carbon System," Bureau of Standards, Scientific Papers, No. 464, Vol. 18, 1923, p. 637.

[5]Marie L. V. Gayler, "Preparation of Pure Manganese," *Journal*, Iron and Steel Institute, Vol. 115, 1927, p. 393.

arise, and it is frequently impossible to determine the source of error. When the program for the study of the iron-manganese-carbon system was laid out, two things were kept in mind; one was to prepare as pure alloys as was possible, without falling too far behind in the melting program, and the other was to study as many of the properties of the alloys as possible. Progress has necessarily been slow because of the readiness with which manganese reacts with oxygen and nitrogen and because of its relatively high volatility and consequent rapid vaporization when heated in vacuo. These difficulties made it necessary to design and build special equipment. All the manganese used in the preparation of the alloys was purified by distillation in vacuo and the alloys were melted under an inert gas atmosphere. Studies of the alloys at elevated temperatures must be carried out in vacuo or under an inert gas atmosphere. The problem is further complicated because the alloys readily attack silica, making it necessary to use silica-free refractories throughout the work.

Materials Used

The manganese used in the preparation of the alloys was distilled in the furnace described by Friauf.[6] A five-pound charge of "thermit" manganese (95 to 97 per cent) yielded two pounds of distillate of satisfactory purity.

The electrolytic iron used was produced by the Niagara Electrolytic Iron Company and according to their analysis contained carbon 0.010 per cent, sulphur 0.003 per cent, phosphorus 0.003 per cent, silicon 0.003 per cent, and copper 0.010 per cent. Spectroscopic examination of this iron showed that it was unusually pure electrolytic iron. Cleaning of the electrolytic iron was effected in some cases by grinding off the oxide on the surface and in others by pickling in hydrochloric acid. The iron, after cleaning, was melted in the vacuum high frequency induction furnace with sufficient carbon to combine with the small percentage of oxygen usually found in electrolytic iron. The pressure in the vacuum furnace was less than 0.01 millimeter when the power was shut off at the conclusion of the melt. The iron then contained 0.01 or 0.02 per cent carbon. It seemed better to retain a small amount of carbon than to have an unknown amount of oxygen. In some cases it should be possible to estimate

[6] James B. Friauf, "The Purification of Manganese by Distillation," Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 1248.

the effect of small amounts of carbon by comparison with the effect of larger percentages.

The iron-carbon alloys were prepared by melting electrolytic iron in an open induction furnace under an atmosphere of natural gas. When no addition of carbon was made, about 0.8 per cent carbon was picked up from the gas. It was usual, however, to add enough sugar

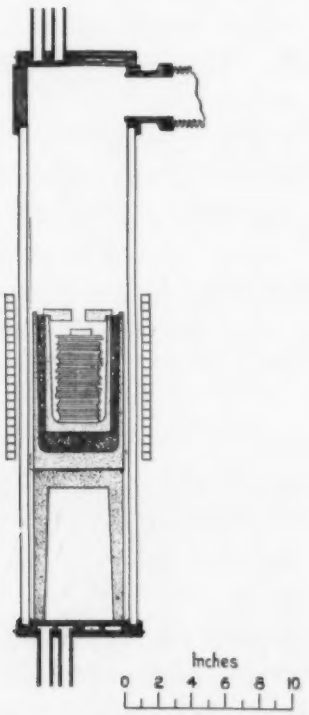

Fig. 1—Vacuum High Frequency Induction Furnace with a Charge of Electrolytic Iron.

charcoal to secure an alloy containing about 4 per cent carbon. The natural gas, when tested, was found to be free from sulphur. The iron-carbon alloys also were remelted in the vacuum furnace. The pressure at the conclusion of the melt was not as low as in the case of the low carbon alloys. The yield from the vacuum melting of the electrolytic iron was low—about five pounds was packed in the crucible and about three melted. Sublimation of the iron accounted to some extent for the sticking of the iron to the top of the crucible. The high carbon iron melts usually were completely melted in the vacuum furnace.

Crucibles

The practice in preparing crucibles is, in general, that recommended by the Bureau of Standards.[7] The material from which the crucibles were prepared was chemically pure magnesium oxide. The magnesium oxide, as received from the manufacturer, was packed in a large graphite crucible. The process of packing (dry packing) reduced the volume 75 per cent. It was then fired in a high frequency induction furnace to as high a temperature as that used for firing the crucibles; there was a further shrinkage of some 80 per cent. This material was ground in a ball mill with flint balls to a fineness of 75 to 200 mesh. The finely divided magnesium oxide was usually moistened with a 50 per cent solution of magnesium chloride. Just enough of the solution was added so that the magnesium oxide particles stuck together when squeezed between the fingers. It was then packed in a graphite crucible around a split, wooden form which could be withdrawn after the packing was completed. The crucibles used in melting the alloys were about six inches deep and 3¼ inches in diameter. The outside was cylindrical while the inside was slightly tapered in order to give a greater wall thickness at the bottom. With crucibles of this size, it is difficult to withdraw a one-piece mandrel, although this method is entirely practical for crucibles of smaller diameter.

The furnace used for firing the crucibles is shown in Fig. 1. The large outer crucible serves as the heater and, while the graphite crucible containing the magnesium oxide crucible to be fired might have been packed directly in the lampblack which is used for thermal insulation, packing and unpacking the furnace would then have been a messy operation and venting the furnace could not have been done as conveniently as in the method which was adopted. In firing the crucibles, the power was started at 8 kilowatts and held until the interior of the furnace was bright red, then the power was raised and held until a vigorous sodium flame appeared at the top of the chimney. The power was increased again when the flame became white, indicating that the reaction between the magnesia and the graphite had started,[8] and held at 14 kilowatts until the reduction of

[7] Louis Jordan, A. A. Peterson, and L. H. Phelps, "Refractories for Melting Pure Metals, Iron, Nickel, Platinum," *Transactions*, American Electrochemical Society, Vol. 50, 1926, p. 155.

[8] Paul Lebeau, "Sur la Réduction de la Magnésie par le Charbon," *Comptes Rendus*, Vol. 144, 1907, p. 799.

the magnesium oxide had become so vigorous that the chimney came clogged two or three times by the magnesium oxide formed contact with the air. This description of the firing operation should make it obvious that no definite information could be obtained in regard to the temperature at which the crucibles were fired. The crucibles were allowed to cool in the furnace over night.

The firing shrinkage of well-sintered, closely packed material

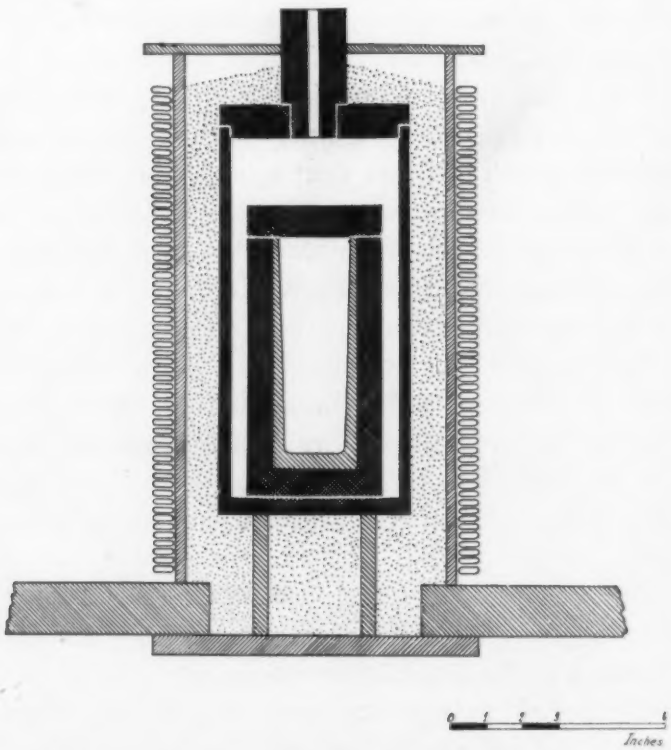

Fig. 2—One of the High Frequency Induction Furnaces Used for Firing the Magnesium Oxide Crucibles. The Cross-Section Shows a Crucible Ready for Firing.

amounted to about 7 per cent of the diameter of the crucible, so that there was no difficulty in withdrawing the fired crucibles from reasonably good graphite forms.

The crucibles could be used only once since all the melts were furnace-cooled and the unusually large thermal expansion of the magnesium oxide caused the crucible, on cooling, either to crack or to be in such a strained condition that it was practically impossible to remove the ingot without destroying the crucible. Crucibles which were used for iron-manganese melts were reground and again made

crucibles. The average loss in magnesium oxide was about 10 cent.

Recently, considerable trouble was experienced with the spalling of the crucibles on the inside. To remedy this difficulty, various methods were tried: varnishing the wooden form and polishing the inside of the graphite crucible, the use of dilute hydrochloric acid and of sodium chloride instead of magnesium chloride in moistening the magnesium oxide before packing. Each of these remedies was successful the first two or three times that it was tried and then the trouble reappeared. Finally, it was found that the addition of about 0.5 per cent of borax as a binder in addition to the usual quantity of magnesium chloride overcame the spalling. Spectroscopic analyses of typical melts made in crucibles prepared with borax failed to reveal any boron pick-up.

Two high frequency induction furnaces were used for crucible firing, one in which the lining graphite crucible was 6x12 inches and the other in which the lining crucible was 8x14 inches. The larger furnace was used for firing the crucibles used in manganese distillation and the outer magnesite crucibles used for protection and thermal insulation in the vacuum furnace. The firing time for this furnace was about two hours, although the crucibles fired in it were not carried to so high a temperature as was used for the crucibles prepared for melting.

Description of the Argon Furnace

The furnace used for the preparation of the alloys consists of a fused quartz tube, 24 inches long and 10 inches in diameter, closed at the bottom by a water-cooled brass casting and at the top by a brass ring and a water-cooled cover. The bottom and the ring are sealed to the silica pipe by means of a vacuum treated, gutta-percha, resin cement. Between the ring and the cover is a ground joint which is sealed with stop-cock grease. The coil has three water connections which are led out through the side of the silica pipe through one-inch holes. These outlets are sealed by rubber gaskets, made vacuum-tight by shellac, if necessary. The coil rests on a fused quartz plate which is supported on a magnesite cylinder. Zirconium silicate cement is used to separate the turns of the coil, is smeared over the coil inside and outside, and is used to close the space between the bottom of the coil and the quartz plate. The cover contains a glass-covered peep-

hole in the center and the outlet to the vacuum pump and the argon purification system. It would have been better had this outlet been in the bottom plate, since if it were in this position, it would be unnecessary to disturb this connection in opening the furnace, and a larger tube could be used than is convenient when it has to be flexible. In charging the furnace, the crucible was placed in the center of the

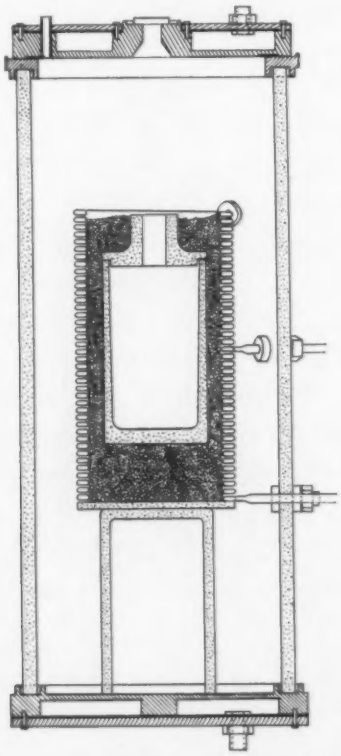

Fig. 3—High Frequency Induction Furnace Used for Melting Under a Controlled Gas Atmosphere.

coil and the pieces constituting the charge packed into the crucible in such a manner as to insure their settling as the melting progressed. The necessity for careful arrangement of the charge is well recognized by every user of high frequency induction furnaces. It is especially important in the case of vacuum melting or in a furnace such as this where it is impossible to push the charge down during the course of the melt. The crucible was covered with a lid having a chimney two inches high. Twenty mesh electrically fused alumina was packed on all sides of the crucible and on the cover. Experience with the vacuum furnace shows that the fused alumina adsorbs much less gas than fused magnesia.

When the furnace was closed, it was evacuated to about 1 millimeter and filled with purified argon; 8 kilowatts were applied for about ten minutes. This was sufficient to bring the charge to a red heat. The furnace was again evacuated and filled with argon to a pressure of a few centimeters less than atmospheric pressure. This slight difference in pressure was sufficient to prevent any sudden heating of the gas in the furnace from lifting up the cover and contaminating the argon. The power input was started at 8 kilowatts and raised 2 kilowatts every ten minutes until between 14 or 16 kilowatts were reached, depending on the melting point of the charge. The power was held constant until the charge was completely molten, continued for five or ten minutes thereafter to insure mixing, and then reduced to a value which would hold the melt just below its freezing point. Power was held at this point for fifteen or twenty minutes and then cut off. The melt could be removed about two hours after the power was shut off.

Those ingots, made in crucibles covered with a lid containing a peep-hole, had pipes at the side of the ingot while the melts made with a crucible entirely surrounded by alundum were free from them. However, when melting is carried out blindly, the charge may not be completely melted, or if the power is kept on long enough to insure complete melting, the temperature is likely to go so high as to cause contamination of the melt by the crucible, as was the case in two or three preliminary runs made with completely covered crucibles.

The largest melt which can be made in this apparatus, with the assurance that all the charge will drop into the melt, is five pounds. The smallest melt which can be made reliably is two pounds. The smaller melts were made in the high manganese range to economize on manganese and because the studies which could be made of these alloys were limited. If the melting went according to schedule, the loss of manganese by vaporization and of carbon through reaction with the crucible were fairly predictable. In weighing up the charge, an allowance for the loss of 0.1 per cent carbon was made (0.1 per cent of the total charge) and for a loss of 10 per cent of the manganese charged. A list of the melts[9] which we have made is given in Table I.

Carbon was determined by the ordinary direct combustion

[9]Melts A-1 to A-36 were analyzed by Mr. Maxwell Gensamer, and melts A-37 to H-2 were analyzed by Mr. Cyril Wells. Mr. Gensamer and Mr. Wells assisted in their preparation.

Table I
Alloys Made 1929-1931

Alloy	Per Cent Carbon		Per Cent Manganese		
	Top	Bottom	Top	Bottom	
A-1	0.008	0.006	1.87	1.99	F[a]
A-2	0.012	0.015	7.17	7.29	F
A-3	0.015	0.013	1.69	1.75	F
A-4	0.020	0.020	4.41	4.46	F
A-5	0.042	0.040	10.17	10.24	F
A-6	0.017	0.016	20.15	20.62	F
A-7	0.029	0.028	13.14	13.03	F
A-8	0.021	0.020	16.10	15.79	F
A-9	0.015	0.013	25.76	25.85	F
A-10			72.4		B[b]
A-11		0.022	67.7		D[c]
A-12		0.012	74.6		B
A-13		0.008	84.0		B
A-14			100.0		B
A-16		1.57	13.00		S[d]
A-17		0.010	1.42		F
A-18		0.014	39.9		F
A-19		0.03	31.9		D
A-20		0.008	36.6		D
A-21		0.02	48.4		D
A-23	0.24	0.24	13.05	13.33	F
A-24		0.34	4.68		F
A-25		0.003	55.0		D
A-26		0.03	60.4		D
A-27		0.01	90.0		B
A-28		0.015	94.4		B
A-29		0.39	7.39		F
A-30		0.01	99.2		B
A-31		0.29	10.22		F
A-32		0.01	2.07		F
A-33		0.31	16.24		F
A-34		0.35	1.90		F
A-35		0.27	20.07		F
A-36		0.82	13.15		F
A-38	0.68	0.76	9.21	9.34	F
A-39	1.26	1.25	10.45	10.43	F
A-40	0.021	0.021	29.16	29.27	F
A-41	0.015	0.015	10.30	10.44	F
A-42	0.44	0.47	12.76	12.92	F
A-43	1.09	0.93	11.97	11.98	F
A-44	1.21	1.15	15.78	15.70	F
A-45	1.03	1.27	12.88	13.26	F
A-47	0.025	0.016	1.10	1.10	F
H-1	1.34	1.39	10.54	10.68	F
H-2	0.47	0.51	9.51	9.79	F

a. F—used drillings from forged bar.
b. B—pulverized sample used.
c. D—drillings from ingot used.
d. S—used thin slice sample.

method, using ascarite for absorbing the carbon dioxide. The blank, usually of the order of about 0.2 milligrams, was determined and subtracted.

The method used for the determination of manganese is that of the Bureau of Standards[10] for the analysis of spiegeleisen. The method is a modification of the bismuthate method as described by

[10] "Modified Bismuthate Method for the Determination of Manganese in Spiegeleisen," Bureau of Standards certificate of analyses for Standard Sample No. 66, Spiegeleisen, February 11, 1925.

Cunningham and Coltman.[11] In the case of the pure alloys, the solution of the sample was easily accomplished by dissolving directly in nitric acid (sp. gr. 1.135). The remaining procedure was practically the same as given by Cunningham and Coltman.

Analyses for carbon and manganese were made on all the alloys,

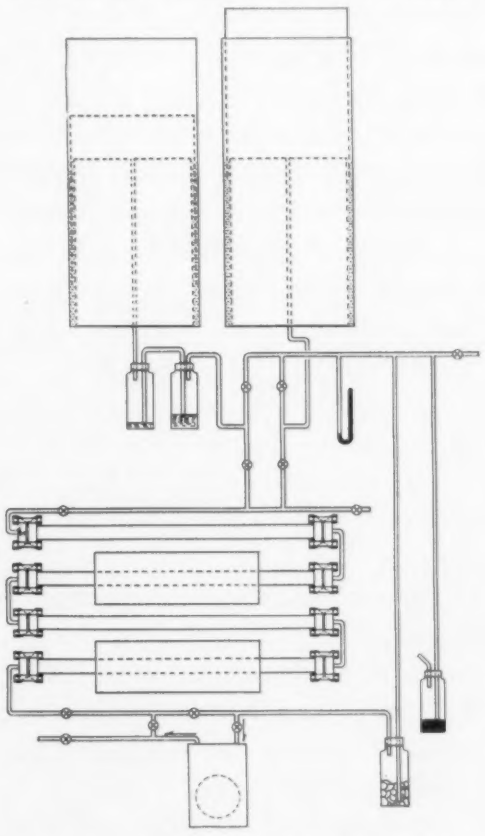

Fig. 4—Apparatus for the Purification and Storage of Helium and Argon.

and carefully checked. Checks within 0.5 milligram of manganese and within 0.5 milligram of carbon dioxide were considered satisfactory.

Sulphur, phosphorus, and silicon were present in such small amounts that they could not be estimated by the ordinary standard chemical methods.

Purification of Inert Gases

The argon and the helium as received, were said to contain about

[11] T. R. Cunningham and R. W. Coltman, "The Determination of Manganese. Part I. A Study of the Bismuthate Method," *Industrial and Engineering Chemistry*, Vol. 16, 1924, p. 58.

three per cent of impurities, principally nitrogen. To remove oxygen and nitrogen, the gas was passed over red-hot shavings of metallic calcium. To take care of hydrogen and carbon monoxide which might be produced in the melting furnace, the gas was also passed over red-hot copper oxide and thence over absorbents for water and carbon dioxide. To remove hydrocarbons from the helium, the copper oxide was raised to a higher temperature. The first apparatus made for this purpose was designed and built by Dr. Friauf using glass throughout, except for the gas holders and the furnaces for the calcium and copper oxide which were wound on seamless steel tubing. The second apparatus is built up from ⅜-inch copper tubing put together with standard fittings. Considerable difficulty was experienced in securing vacuum-tight connections. It was necessary to grind-in the valves by means of pumice and almost all the joints had to be shellacked. The advantages of the metal system lie in its greater ruggedness and in the larger internal diameter of the tubing. The system of tubing shown in the diagram was designed so that the gas could be taken from or returned to either tank and so that the gas could be passed from one tank to the other through the purification system.

The closed-end manometer is used to observe the pressure in the system and is independent of atmospheric pressure, while the other pressure gage is useful in indicating whether the system being evacuated is tight in a shorter time than would be required if it were necessary to wait until a vacuum had been obtained which could be observed on the closed-end manometer.

In the second apparatus, the furnaces and tubes for absorbents were closed by standard flanges and lead gaskets.

The rotary oil pump used for evacuating the furnace and transfering the gas from one holder to another was of the vacuum-pressure type so that the gas could be withdrawn from the furnace, purified, and used again.

Effect of Gases

No pick-up of argon by the melts has yet been detected. However, no test was carried out except in the case of pure iron. A sample melted under argon was analyzed for gases by the Bureau of Standards, and no argon detected. Alloys containing high manganese are so troublesome in gas analysis by the vacuum fusion method

that it is impracticable to analyze the alloys containing manganese. The melts H-1 and H-2 seemed to require a definitely greater power input for melting than similar alloys melted under argon. This, of course, is not unexpected in view of the fact that helium has a thermal conductivity some nine times as great as that of argon.[12]

Nitrogen is to be avoided in the preparation of manganese alloys. It reacts readily with manganese at elevated temperatures, forming nitrides. One melt of distilled manganese under argon was contaminated by the accidental presence of a small amount of nitrogen and was sufficiently magnetic to be attracted by a small magnet.

Forgeability

By careful attention to forging temperature, all melts below and including that containing 40 per cent manganese have been forged. There is, however, no reason for believing that the alloys between 40 and 65 per cent could not be forged. The low carbon iron-manganese alloys could be forged more easily and at higher temperatures than the high carbon alloys.

The low carbon iron-manganese alloys were sawed with little difficulty except those containing from 10 to 20 per cent manganese. The alloys containing from 70 to 100 per cent manganese were decidedly brittle, many of them showing a conchoidal fracture, characteristic of intermetallic compounds.

[12]Walter Schwarze, "Bestimmung der Waermeleitungsfaehigkeit von Argon und Helium nach der Methode von Schleiermacher." *Annalen der Physik*, Vol. 11, 1903, p. 303.

ALLOYS OF IRON, MANGANESE AND CARBON—Part II

Thermal Analysis of the Binary Alloys

By Francis M. Walters, Jr., and Cyril Wells

Abstract

A gradient furnace with certain novel features was used for the thermal analysis of high purity, iron-manganese alloys containing from 0 to 60 per cent manganese.

In general, the results agree with those of previous investigators. The low temperature transformations, however, were found definitely in 13 to 20 per cent manganese alloys on both heating and cooling, and it was established by thermal analysis that the alpha to gamma transformation in the 13 per cent alloy takes place above 600 degrees Cent. (1110 degrees Fahr.).

Introduction

THERMAL analysis is so fundamental and important a method for the observation of phase changes that it is usually the first and sometimes the only method, other than microscopy, employed in the study of an alloy system. Consequently, after microscopic examination, it was the first method applied to the study of the high purity iron-manganese alloys (carbon 0.02 per cent or less), the preparation of which is described elsewhere.[1]

Apparatus

With the gradient furnace of Rosenhain[2] uniform rates of heating and cooling may be obtained over a large range of temperature. The data, when plotted as inverse rate curves, are easy to interpret.

The design of the gradient furnace used (Fig. 1) followed the

[1]Francis M. Walters, Jr., "Alloys of Iron, Manganese, and Carbon. Part I. Preparation of the Alloys," Transactions, American Society for Steel Treating, May, 1932, p. 577.

[2]Walter Rosenhain, "Some Appliances for Metallographic Research", *Journal,* Institute of Metals, Vol. 13, 1915, p. 160.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931, of the authors, Francis M. Walters, Jr., is a member of the society and director of the Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh and Cyril Wells, an assistant metallurgist in the Bureau. Manuscript received June 9, 1931.

modification developed by the Bureau of Standards.[3] An alundum tube 23 inches long is closed at the upper end, with a heating element of platinum wound on the upper three inches, and is cooled at the

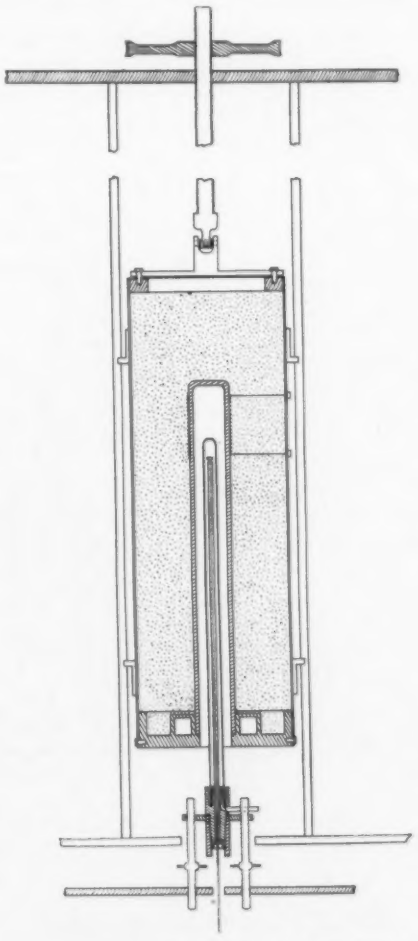

Fig. 1—Section of Gradient Furnace. The Furnace is Moved by the Screw, While the Sample Remains Stationary.

lower end by circulating water. Thermal insulation is furnished by three and one-half inches of carefully packed calcined infusorial earth. The specimen, which is about 0.5 inch in diameter and 0.125 inch or less in thickness, is attached to the thermocouple by lightly pounding the thermocouple bead into a saw cut extending to the center of the sample. The sample is supported by the two-hole refractory tube through which the thermocouple wires are run, and is

[3] H. Scott and J. R. Freeman, Jr., "Use of a Modified Rosenhain Furnace for Thermal Analysis," Bureau of Standards Scientific Papers, No. 348, Vol. 15, 1919, p. 317.

enclosed by a fused quartz tube, the upper part of which is transparent. The quartz tube is sealed into the brass holder with paraffin, and the thermocouple wires are sealed with a gutta-percha vacuum cement. The furnace is moved relative to the sample by a screw which is driven, through gear reduction, by a $\frac{1}{10}$ horse power synchronous motor. Keeping the sample stationary has the advantage

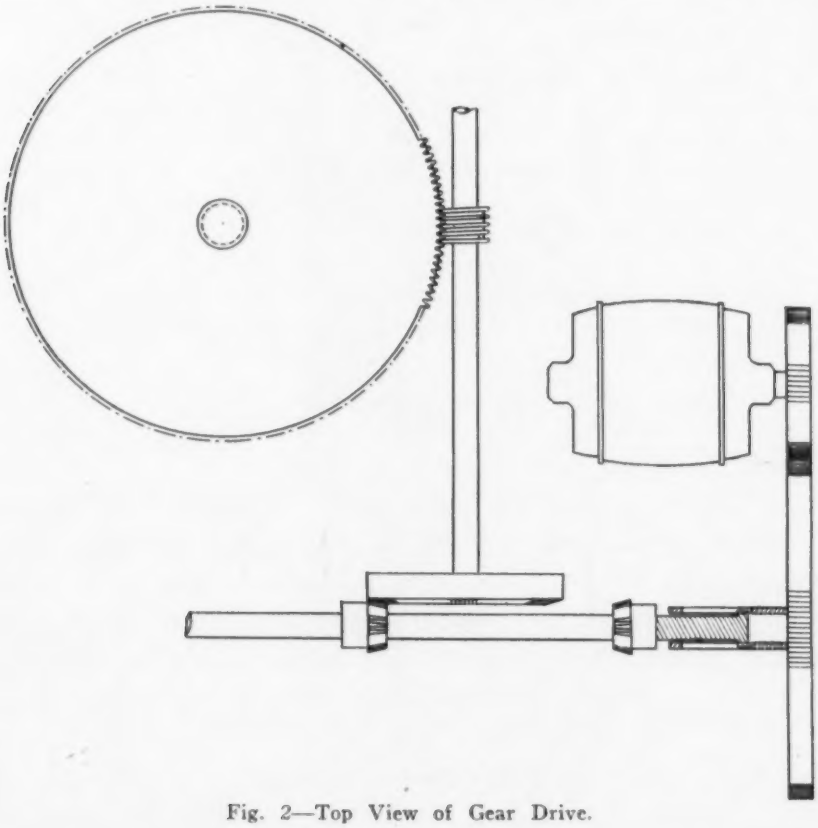

Fig. 2—Top View of Gear Drive.

that a larger outlet to the vacuum pump may be used. The motor drive was adopted because it appeared to be easier to construct than a satisfactory hydraulic drive. In designing the drive for the furnace, several considerations must be kept in mind; the direction of travel of the furnace should be easily reversible; there should be various speeds of travel; and, if commercial gears are used, worm gears should be used for the final reduction. The arrangement shown in Fig. 2 has the disadvantage of being rather noisy and of producing so much vibration that it was necessary to support the thermocouple and sample directly from the floor. While provision was made for a change in the rate of heating and cooling, a single rate of

about four seconds per degree Cent. was used throughout the work. The furnace moves a quarter of an inch per minute.

A 50-tooth worm gear has been applied to a type "K" potentiometer so that one complete revolution of the worm changes the setting of the potentiometer 0.02 millivolt. When the high sensitivity galvanometer comes to the null position, it illuminates a vacuum-type

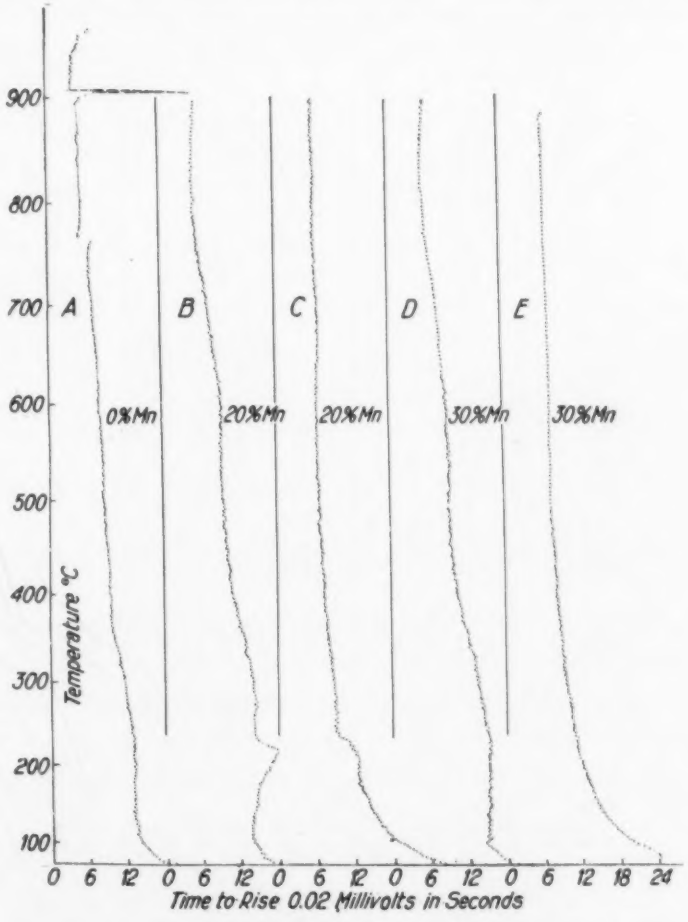

Fig. 3—Typical Heating Curves. A, B and D are with a Nickel Tube Around the Alundum Tube. C and E are Without the Nickel Tube.

photoelectric cell, whose response is amplified by a grid-glow tube, which actuates the chronograph relay. (The photoelectric cell materially decreases fatigue in making the observations). The chronograph is driven by a 1/40 horse power synchronous motor; the drum is about six inches in diameter and is long enough to record observations lasting 160 minutes. The chronograph record sheet is read to one-thousandth of a minute by means of a special scale, the length of

which is equal to the circumference of the chronograph drum, and which is divided into two hundred parts. No time signals are placed on the chronograph record since the frequency of the alternating current is sufficiently constant.

The power used to heat the furnace was not controlled for the observations reported in this paper. The use of a temperature con-

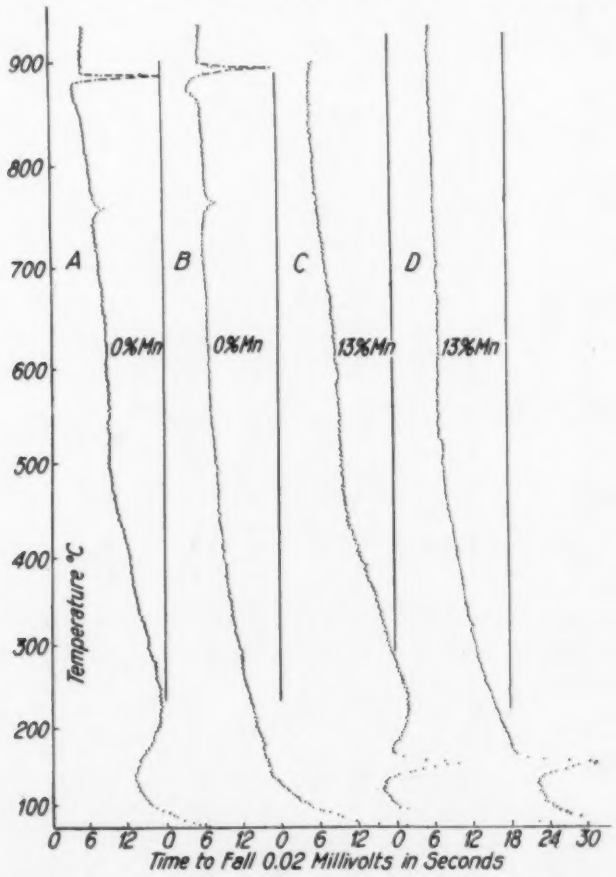

Fig. 4—Typical Cooling Curves. A and C with the Nickel Tube and B and D Without.

trol which employs the platinum heating unit as one arm of a Wheatstone bridge is contemplated.

The galvanometer used had a period of 8.4 seconds and a sensitivity better than 0.1 microvolt. As the time between readings approached the period of the galvanometer, the readings became irregular and, at the higher temperatures, better curves were obtained by observing the time for the temperature to rise or fall the equivalent of 0.04 instead of 0.02 millivolt.

In an attempt to improve the gradient in the furnace, a nickel tube was placed outside of the alundum tube. The metal tube was held about a sixteenth of an inch away from the alundum tube by wedges at the top and bottom and was not in direct contact with the water-cooled plate at the bottom. The poorer gradient (Figs. 3 and 4) obtained above 300 degrees Cent. (570 degrees Fahr.) is probably due to the high conductivity of the nickel and below this temperature to the lack of thermal contact with the water-cooled portion of the furnace.

To check the performance of the equipment, several runs were

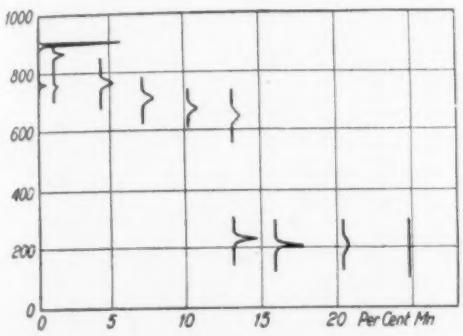

Fig. 5—Diagrammatic Representation of Transformation Points on Heating.

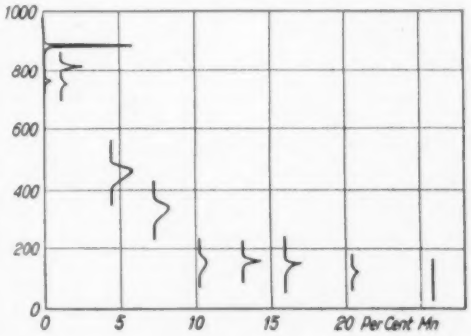

Fig. 6—Diagrammatic Representation of Transformation Points on Cooling.

made on vacuum-melted electrolytic iron which contained less than 0.02 per cent carbon. The results agreed satisfactorily with those of other observers both in regard to the magnitude of the effects observed and the temperatures at which they occurred. Runs made at various times showed satisfactory reproducibility.

Results

The data obtained for the low carbon iron-manganese alloys are shown graphically in Fig. 5 and 6. An attempt has been made to indicate the character of the thermal disturbance as well as the temperature at which it occurs. The maximum plotted for each transformation point is the ratio of the greatest excursion (in terms of the heating or cooling rate scale), minus the rate of cooling, to the rate of cooling. This procedure was followed in an attempt to make possible a comparison of the magnitudes.

In comparing the results with those of previous investigators, the effect of the relatively small amounts of carbon and other impurities

present, even in Hadfield's alloys,[4] is evident, particularly in the range from 10 to 20 per cent.

For alloys up to ten per cent manganese, the lowering of the alpha-gamma transformation on heating indicates that the effect of manganese is to render the gamma phase more stable. The temperature at which the gamma-alpha change occurs on cooling is considerably below the reverse transformation. This may be ascribed to

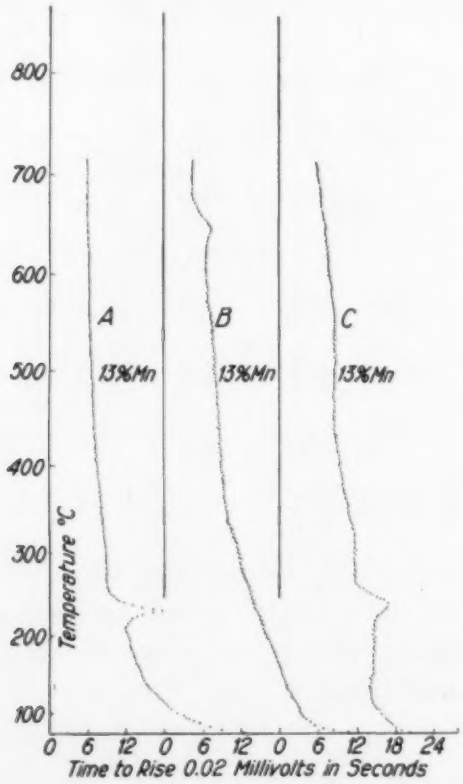

Fig. 7—Heating Curves of 13 Per Cent Manganese Alloy After Various Treatments. A. As-forged. B. Cold-worked and soaked at 575 degrees Cent. for 50 hours. C. After a Slow Cool Lasting a Week.

"sluggishness," although the authors have yet no direct experimental evidence which shows that the transformation will occur at a higher temperature if given time. That the magnitude of the disturbance is greater on cooling than on heating, the authors ascribe to a greater energy change rather than to experimental error, since the volume

[4]Sir Robert Hadfield, "Alloys of Iron and Manganese Containing Low Carbon," *Journal*, Iron and Steel Institute, Vol. 115, 1927, p. 297.

change for the gamma to alpha transformation is greater than that for alpha to gamma.[5]

The transformations become less sharp and spread over a greater temperature range as the manganese content increases to ten per cent. At 13 per cent, they again become sharp, and additional evidence is scarcely needed to show that the transformations occurring in the 13 and 16 per cent alloys at low temperatures are decidedly different

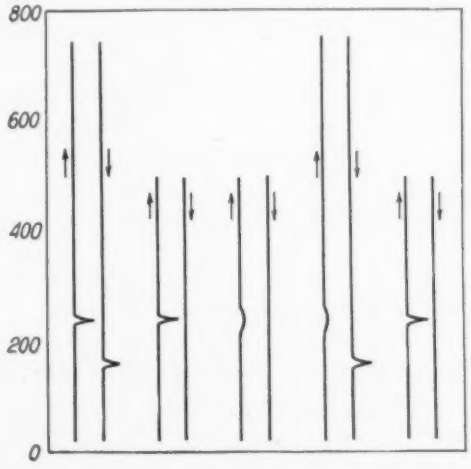

Fig. 8—Diagram of a Series of Runs, Which Show That it is Necessary to Take the 13 Per Cent Manganese Alloy Above 650 Degrees Cent. to Secure Low Temperature Transformation Points.

in character. In the case of the 13 per cent alloy, this has been shown in two other ways by thermal analysis. This alloy in the "as-forged" condition, showed only low temperature points, but, after cold working and soaking at 575 degrees Cent. (1070 degrees Fahr.) for fifty hours, it showed a transformation at about 650 degrees Cent. (1200 degrees Fahr.) a temperature which lies on the continuation of the alpha-gamma transformation curve for the alloys containing less manganese. Curve "C" of Fig. 7, taken of the 13 per cent alloy after a cooling from 1000 degrees Cent. (1830 degrees Fahr.), which lasted a week, indicates that no transformation of gamma to alpha had taken place.

That the alpha-gamma transformation takes place at about 650 degrees Cent. (1200 degrees Fahr.) is indicated also by the series of runs shown diagrammatically in Fig. 8. Unless the 13 per cent alloy

[5]Francis M. Walters, Jr., and Maxwell Gensamer, "The Alloys of Iron, Manganese, and Carbon. Part IV. A Dilatometric Study of the Binary Alloys", TRANSACTIONS, American Society for Steel Treating, May, 1932, p. 608.

is heated above 650 degrees Cent. (1200 degrees Fahr.), the low temperature transformations are almost completely suppressed, which would not be likely if they were complementary. The dilatometric observations indicate that these transformations involve the epsilon transformation.

The low temperature thermal disturbances have been observed, at progressively lowered temperatures, for both the 16 and 20 per cent alloys. From 26 to 60 per cent manganese, no definite thermal disturbance has been detected.

ALLOYS OF IRON, MANGANESE AND CARBON—Part III

An X-ray Study of the Binary Iron-Manganese Alloys

By M. Gensamer, John F. Eckel, and F. M. Walters, Jr.

Abstract

A systematic X-ray investigation of the low carbon iron-manganese alloys confirms in general the work of Schmidt and of Öhman.

A comparison of cold-worked specimens with those prepared in a manner to avoid cold working as far as possible showed that the formation of the hexagonal close-packed phase is favored by stress. In some alloys this phase appears on quenching; but is absent when slowly cooled.

Introduction

AS PART of the program of a systematic investigation of the iron-manganese-carbon system, a number of iron-manganese alloys (carbon 0.02 per cent or less) have been studied by the Debye-Hull method of X-ray crystallographic analysis. Although two excellent studies of the system have been made by Schmidt[1] in Germany and by Öhman[2] in Sweden, it was considered desirable to present the results of this investigation, calling attention to their work, and presenting some new material.

The crystal structure of iron is familiar to all, but it may be well to review the work on manganese and on iron-manganese alloys. Manganese exists in three allotropic modifications[3, 4]. Alpha manga-

[1]Winfried Schmidt, "X-ray Investigation of the Iron-Manganese System", *Archiv für das Eisenhüttenwesen*, 3, 293, 1929 (Heft 4, October 1929).

[2]Einar Öhman, "X-ray Investigation of the Iron-Manganese System", *Zeitschrift für physikalische Chemie*, Abt. B, 8 Band, Heft 1/2, June 1930, p. 81.

[3]Arne Westgren and Gösta Phragmen, "Zum Kristallbau des Mangans", *Zeitschrift für Physik*, Vol. 33, 1925, pp. 777-788.

[4]A. J. Bradley, "The Allotropy of Manganese," *Philosophical Magazine*, Vol. 50, Ser. 6, 1925, p. 1018.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. All of the authors are members of the society. M. Gensamer is assistant metallurgist, John F. Eckel, research assistant and F. M. Walters, Jr., director of the Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 9, 1931.

nese,[2] stable from room temperature to 724 degrees Cent. (1335 degrees Fahr.) is extremely complex,[5] having 58 atoms in the unit cell[6, 7] arranged in a body-centered cubic lattice with 29 atoms in a group at each lattice point; the side of the unit cell is 8.894 ± 0.005 Å. Beta manganese,[2] stable from 742 to 1191 degrees Cent. (1368 to 2175 degrees Fahr.) is cubic with 20 atoms in the unit cell[8] and 6.29 Å for the side of the unit cell. Gamma manganese, stable from 1191 degrees Cent. (2175 degrees Fahr.) to the melting point at 1245 degrees Cent. (2273 degrees Fahr.), has been considered to be face-centered tetragonal in structure with 4 atoms in the unit cell, whose base is 3.774 ± 0.003 Å, with an axial ratio of 0.937; this is the structure of freshly prepared electrolytic manganese. Schmidt,[1] investigating the iron-manganese system, found five phases occurring at ordinary temperatures. Alpha iron (body-centered cubic) occurs in alloys containing from 0 per cent to 20 per cent manganese. He discovered a new phase appearing between 12 per cent and 29 per cent manganese, hitherto unsuspected. This phase, which he named epsilon, is hexagonal closepacked. Gamma iron (face-centered cubic) occurs from 16 to 60 per cent manganese; beta manganese occurs from 62 to 98 per cent manganese, with the structure previously described for this phase; alpha manganese, also as previously described, is only obtained at room temperature with very low iron content.

Öhman[2] also investigated this system using purer materials and care in heat treatment. The alloys, prepared from electrolytic iron and manganese distilled in a vacuum carbon resistance furnace, were melted in vacuo. High temperature powder photographs showed the face-centered cubic phase from 0 to 65 manganese, and above 65 per cent, the beta manganese phase. The temperature of transformation of beta manganese to alpha manganese is changed very little by varying the iron content, and at 500 degrees Cent. (930 degrees Fahr.) alpha manganese may contain as much as 35 per cent iron in solution. By quenching the 78.5 per cent manganese alloy from 1150 degrees Cent. (2100 degrees Fahr.), gamma manganese was obtained along

[5]E. C. Bain, "Nature of Solid Solutions", *Chemical and Metallurgical Engineering*, Vol. 28, No. 1, 1923, p. 21.

[6]A. J. Bradley and J. Thewlis, "Crystal Structure of Alpha Manganese", *Proceedings*, Royal Society of London, 115 A, 1927, pp. 456-471.

[7]G. D. Preston, "The Crystal Structure of Alpha Manganese," *Philosophical Magazine*, 1928 (VII) 5, p. 1198.

[8]G. D. Preston, "Crystal Structure of Beta Manganese," *Philosophical Magazine*, 1928 (VII) 5, p. 1207.

with beta manganese. With increasing iron content, the axial ratio for gamma manganese approaches unity. Schmidt's epsilon phase (hexagonal close-packed) was confirmed, but Öhman states that it does not occur alone. All three phases were found in quenched specimens and he states that it is only in these quenched specimens that the epsilon phase occurs, from which he concluded that it is a transition phase occurring during the change from gamma to alpha iron. Face-centered gamma iron and face-centered gamma manganese probably form a continuous series of solid solutions. This system has also been studied by Atomi Osawa.[9]

First Method of Investigation

The iron-manganese alloys used in the present study contained about 0.02 per cent carbon.[10] Powder photographs were made using a cylindrical camera of about 10 centimeters diameter, with the specimen in the form of a needle of less than one millimeter diameter, rotating concentrically with this cylinder. The needle specimens were prepared by machining the forged bars, and were etched before being photographed. In the case of the brittle alloys, the specimen was powdered to 200 mesh and shaped into a needle using collodion as a binder. (The 72 per cent manganese alloy contained some ductile material which could not be powdered and hence is missing from the structure as determined by X-rays). The camera was calibrated by thinly copper coating a number of machined specimens by immersion in copper sulphate solution, so that a powder photogram of copper was superimposed on the photogram of the specimen. An iron target was used for the iron-rich alloys, and a chromium target (prepared by electrodeposition on a copper base) for the manganese-rich alloys. The tube was a modified Shearer gas tube, permitting close approach to the target and relatively short exposures (2 to 4 hours).

Results with Needle Specimens

The results of this part of the investigation are summarized in Table I, along with the results of previous investigations. They are in agreement with those obtained by Schmidt[1] and Öhman,[2] except

[9]Atomi Osawa, "X-ray Investigation of Iron and Manganese Alloys", *Science Reports*, Tohoku Imperial University, Vol. 19, 1930, p. 247.

[10]Francis M. Walters, Jr., "The Alloys of Iron, Manganese, and Carbon. Part I. Preparation of Alloys", TRANSACTIONS, American Society for Steel Treating, May, 1932, p. 577.

Table I
Lattice Dimensions of Iron-Manganese Alloys

% Mn	α-Fe a	Epsilon a	Epsilon c/a	γ-Fe a	γ-Mn a	γ-Mn c/a	β-Mn a	α-Mn a	Observer
0.0	2.857								Schmidt
2.0	2.860								Friauf
3.7	2.861								Öhman
4.4	2.863								Friauf
7.0	2.861			3.595					Öhman
7.2	2.864								Friauf
9.1	2.860			3.588					Öhman
	2.867			3.606					
10.2	2.868	2.520	1.615						Friauf
12.1		2.532	1.604						Schmidt
13.1	2.870	2.526	1.612	3.581					Friauf
15.2	2.859			3.603					Öhman
	2.865			3.582					
16				3.586					Schmidt
16.0	2.881	2.531	1.613	3.589					Friauf
20	2.871								Schmidt
20.4		2.536	1.611						Friauf
22.9	2.866	2.541	1.616	3.595					Öhman
				3.603					
25.8		2.535	1.612	3.594					Friauf
29		2.543	1.605						Schmidt
30.7	2.862			3.604					Öhman
				3.603					
39.9				3.616					Friauf
46.6				3.624					Öhman
56.1				3.635					Öhman
58				3.616					Schmidt
63							6.24		Schmidt
63.9				3.647				8.864	Öhman
72.4					3.66	1.01	6.260		B. M. R.
74.5					3.68	1.00	6.261		B. M. R.
78.5					3.705	0.976	6.286	8.877	Öhman
84.0					3.70	1.00	6.283		B. M. R.
87							6.28		Schmidt
90.0					3.71	1.00	6.297		B. M. R.
91.4							6.297	8.890	Öhman
94.4					3.73	1.00	6.290		B. M. R.
100								8.89	Schmidt
100							6.305	8.904	Öhman
100								8.897	B. M. R.
100*					3.774	0.937	6.298	8.894	Westgren
100					3.776	0.934			Persson & Öhman
100								8.903	Bradley
100							6.29	8.894	Preston

*γ-Mn electrolytic; β-Mn magnesium reduced.

that the epsilon phase was found in the forged alloys from 10 to 26 per cent manganese, whereas Öhman states that he obtained it only in quenched alloys. It was suspected that this might be the result of the machining operation in the preparation of the specimens. That this treatment does give results which are not representative of the forged alloy has been demonstrated by photographing specimens prepared solely by grinding, using a technique to be described. Öhman states that the gamma phase in alloys containing over 70 per cent manganese is face-centered tetragonal rather than face-centered cubic; he bases this on the structure of quenched specimens. In the present investigation, lines ascribed to this phase have been found in the

photographs of alloys which were cooled in the crucible, from the melting point to room temperature in about two hours. Although the measurement of these lines was difficult as they were weak and diffuse, it appears that in these rather slowly cooled, very low carbon alloys the gamma phase is, within the accuracy of the measurements, face-centered cubic.

The use of the machined needles described above has led to erroneous results as to the true structure of the alloys from which the specimen was prepared. It was suspected that the severe cold working of a metastable phase at ordinary temperatures might cause a decomposition of that phase into a more stable or a transition phase. The X-ray pattern obtained would then be representative of the machined specimen instead of the original condition. The machining of a number of the needles used for X-ray analyses was accomplished only with difficulty. In each case, the needle was severely cold-worked before being completely turned. Hence, it cannot be said that the needles machined from the forged bars are representative of the structure of the "as-forged" alloys.

Edge Method

A different arrangement was used in the latter part of the investigation, to avoid the use of such severely cold-worked specimens and to study the effect of heat treatment. Furthermore, it permitted the use of the same specimens which had been used for metallographic studies of various heat treatments. A plane surface was ground on the side of the specimen in such a way as to make an angle of 90 degrees or less with the surface already prepared for microscopic examination. The specimen was then treated with sulphuric acid with the hope that the acid would dissolve the metal which had been cold-worked during the grinding process. The specimens, thus prepared, were more representative of the original condition than machined needles. They were probably as representative of the desired treatment as a metallographic specimen, since the method of preparation is essentially the same.

The specimen was mounted on the spindle of a modified Dickinson-Henson spectrograph by means of plastilene so that the edge was parallel to the axis of the camera. This edge was centered on the axis of the camera by means of a telescope, by adjusting the position of the specimen on the spindle until no apparent movement of the

edge could be observed as the specimen was rotated. In this position, one-half of the X-ray beam from the pinhole system was stopped by the specimen while the other half of the beam passed. The latter half of the beam was allowed to strike the film for about thirty seconds before the back-stop was placed in position. This produced a spot on the film in the form of a semicircle which was used as the zero point for subsequent measurements; and although in the method of analysis used, this was not relied upon, its position was as nearly correct as that of any of the lines. The specimen was oscillated through an angle of 45 degrees with the prepared edge remaining on

Fig. 1—Typical X-ray Photogram Obtained Using "Edge Method."

the axis of the cylindrical camera. The method materially reduced the exposure required to obtain a suitable pattern. An exposure of about twenty milliampere-hours was required for the machined needle specimen, while the exposure required for the "edge method" averages eleven milliampere-hours. A typical pattern is shown in Fig. 1.

The positions of the lines on the films were measured to 0.1 millimeter, the distance measured being from the straight edge of the semicircular trace of the incident beam to the nearest edge of the line. These positions were plotted as abscissae on strips of coordinate paper, as shown in Fig. 2, "A," "C," and "E." The length of the line drawn at these positions represents the relative intensity of the line of the photogram as estimated from the X-ray pattern on a scale of ½ to 10: the strongest line on the film was assigned an intensity of 10; the weakest line easily measurable, an intensity of 1; weaker lines, an intensity of ½.

The patterns, as plotted, were then fitted to the charts of Fig. 2 until all of the lines had been identified. On charts "B" and "D," the positions of the lines (as calculated from the previous calibration of the camera) were plotted against the lattice parameter. By moving the strips with the line positions over the charts until the best possible match was obtained for all the lines, it was possible to

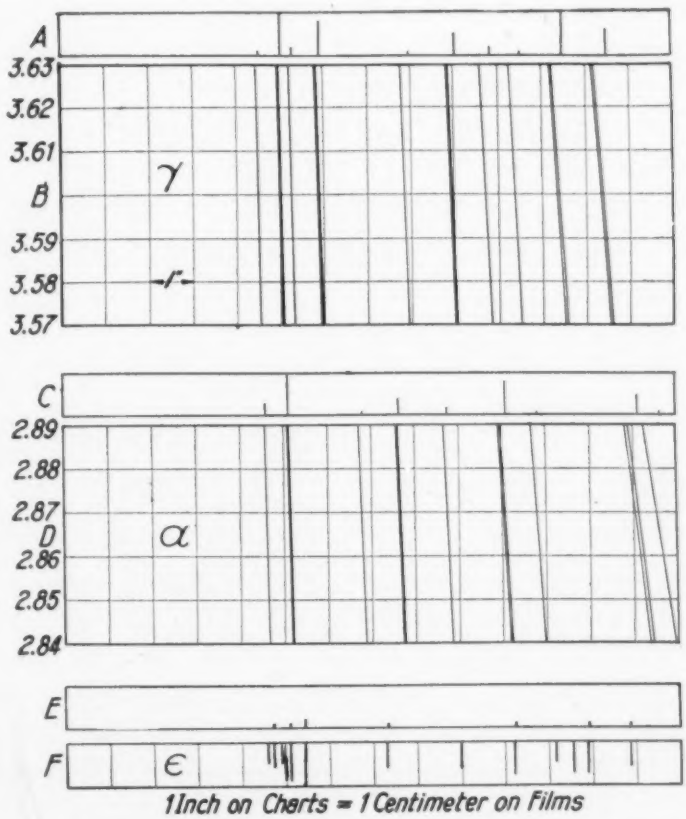

Fig. 2—B, D, and F are Charts by Which the Various Phases Were Identified. A, C, and E are Typical Plots of the Positions of the Lines and Their Relative Intensities.

identify easily and rapidly the various phases present and estimate the dimensions of the unit cell for the two cubic lattices, although this could not be determined with more precision than the second decimal place.

It is obvious that such charts can be prepared only for lattices of the cubic system, since in all other cases at least two dimensions are necessary to describe the unit cell. However, the dimensions of the hexagonal close-packed phase encountered in these alloys remain nearly enough constant to permit the identification of this phase by comparison with the calculated position for one set of lattice dimensions. The results obtained by this method in the study of iron-manganese alloys are summarized in Table II.

It may be seen from this table that the epsilon phase appears over a wide range of composition, and in forged, furnace-cooled, and quenched specimens. The numbers given in the table are the relative

Table II

% Mn	Forged α	Forged ε	Forged γ	Furnace Cooled α	Furnace Cooled ε	Furnace Cooled γ	Quenched α	Quenched ε	Quenched γ	Special α	Special ε	Special γ	Special Treatment
1.7				10			10						
4.4				10		1	10						
7.2				10	1	½	10						
10.2	10		4	10	1	2	10	1					
13.1	10	1	10	10	5	5	10	2	4				
16.0				1	10	5				½	10	6	*1*
20.4		1	10		10	7	2	2	10		10	4	*1*
25.8		1	10		2	10	1	1	10	3	3	10	*2*
31.9					1	10							

1. Furnace cooled, then to —190 degrees Cent. (—310 degrees Fahr.).
2. Very slowly cooled.

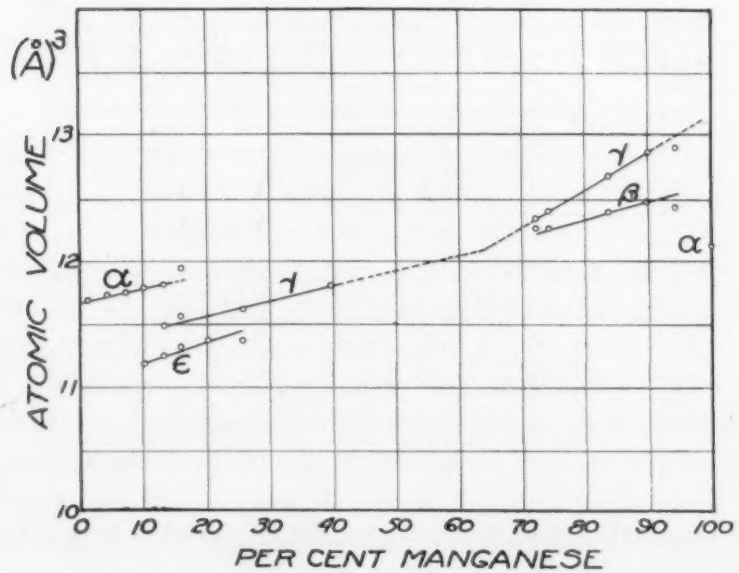

Fig. 3—The Influence of Manganese on the Atomic Volume of the Various Phases Found in the Iron-Manganese System. The Atomic Volumes Were Calculated by Dividing the Volume of the Unit Cell by the Number of Atoms Per Unit Cell. These Data Were Obtained from Machined Needle and Powdered Specimens.

intensities of the strongest lines for each phase appearing in the photogram of each specimen, an intensity of ten being assigned to the strongest line in the photogram; so that the numbers in the table are some measure of the relative amounts of the phases present. The data presented in the table have been summarized graphically in Fig. 4; in these diagrams, the fractional amounts of the three phases de-

scribed, calculated from the intensities shown in Table II, are plotted against the weight per cent of manganese. It is realized that this procedure is highly questionable and certainly not quantitative. These curves indicate that the epsilon phase occurs in larger amounts and with lower manganese contents in the furnace-cooled alloys than in the quenched alloys. The gamma phase is retained at low temperatures with lower manganese contents in the furnace-cooled than in

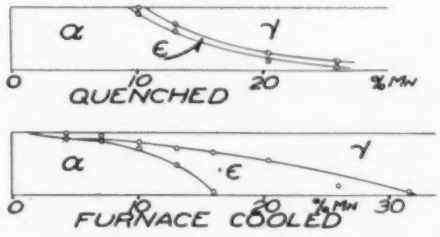

Fig. 4—Graphical Representation of the Fractional Amounts of Each Phase Present in the Furnace-Cooled and Quenched Alloys as Estimated from the Relative Intensities of the Strongest Line of Each Phase.

the quenched alloys. That the epsilon phase is obtained in this series of alloys over a wider range of composition and heat treatment than has been observed by other investigators is believed to be due to their very low carbon contents.

The most interesting point brought out by this investigation is the effect of stress on the structure of these alloys. That the formation of the epsilon phase is favored by stress is seen in the results obtained on ground specimens (the machined needle of the 20 per cent manganese alloy contained only the epsilon phase, while the ground specimen was principally gamma). The presence of some gamma phase in the 4 per cent manganese alloy when slowly cooled, but its absence up to 7 per cent manganese when quenched, demonstrated the effect of manganese on the rate of transformation of the gamma to the alpha phase, and the important part stress plays in this change.

Acknowledgment

The authors desire to acknowledge their indebtedness to Dr. James B. Friauf, who began the investigation and collected most of the data on the low manganese alloys with the Debye set-up, which is of his design and construction.

ALLOYS OF IRON, MANGANESE AND CARBON—Part IV

A Dilatometric Study of Iron-Manganese Binary Alloys

By Francis M. Walters, Jr. and M. Gensamer

Abstract

The dilatometer constructed for the study of the iron-manganese alloys can be used from —200 to 1000 degrees Cent. with the specimen in a vacuum or an inert gas.

The indications of phase changes observed by thermal analysis have been confirmed and extended. The low temperature transformations on cooling of the alloys with thirteen or more per cent manganese may be ascribed to the epsilon phase.

X-ray measurements of lattice dimensions are used in the interpretation of the dilatometric observations.

A preliminary study of the rate of heating and cooling indicates that the rate makes little difference in the temperature at which the transformation begins, but has a marked effect in the transformation range.

Introduction

THIS paper presents the results of dilatometric observations made on a series of iron-manganese alloys (carbon 0.02 per cent or less, with one exception). Their preparation,[1] microstructure, thermal analysis,[3] and X-ray analysis[4] have been elsewhere described.

The dilatometer offers several distinct advantages as an instrument for the observation and study of phase changes. It is not necessary to employ a carefully controlled rate of heating and cooling

[1]Francis M. Walters, Jr., "The Alloys of Iron, Manganese, and Carbon. Part I. Preparation of the Alloys", Transactions, American Society for Steel Treating, May, 1932, p. 577.

[3]Francis M. Walters, Jr., and Cyril Wells, "The Alloys of Iron, Manganese, and Carbon. Part II. Thermal Analysis of the Binary Alloys", Transactions, American Society for Steel Treating, May, 1932, p. 590.

[4]M. Gensamer, John F. Eckel, and Francis M. Walters, Jr., "The Alloys of Iron, Manganese, and Carbon. Part III. An X-ray Study of the Binary Iron-Manganese Alloys", Transactions, American Society for Steel Treating, May, 1932, p. 599.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. Of the authors, who are members of the society, Francis M. Walters, Jr., is director and M. Gensamer is assistant metallurgist, Bureau of Metallurgical Research, Carnegie Institute of Technology, Pittsburgh. Manuscript received June 9, 1931.

as is the case with certain methods of thermal analysis, and it is possible to arrest the observations at any temperature and observe the effect of time upon the transformation. Changes in length are easily observable over a wide range of temperature with the same set-up.

More important still than the advantages just mentioned, is the possibility, in many cases, of correlating the observations made by X-rays on the phases present at high temperatures,[5] or the measurements of lattice dimensions at room temperature, with the changes observed dilatometrically. If X-ray data at the temperature at which the phase change occurs are not available, the lattice dimensions can be corrected to this temperature by the expansion observed. To illustrate the method, consider the change from the gamma phase, which is face-centered cubic, to the epsilon phase, which is hexagonal close-packed, assuming that both phases have the same coefficient of thermal expansion. The atomic volume for the gamma phase is given by $\frac{a^3}{4,}$ and for the epsilon phase by $\frac{0.866\ c.a^2}{2}$ where "a" is the side of the base of the unit cell and "c" is its height. Substituting the values of the lattice dimensions obtained for the 13 per cent manganese alloy,[6] one obtains for the ratio of the sides of the elementary parallelopiped $\frac{L\gamma}{L\epsilon} = \sqrt[3]{\frac{\text{atomic volume } \gamma}{\text{atomic volume } \epsilon}} = 1.0068$. Then the length change expected, since the length change in the specimen being tested should be proportional to that of the elementary parallelopiped, would be a contraction of 0.0068 inch for a one inch specimen in changing from the gamma to the epsilon phase. Let us see how this can be applied to the interpretation of the dilatometric curves. It is known, from a similar consideration, that the change from gamma to alpha, which is body-centered cubic, is an expansion, and from epsilon to alpha a still greater expansion; and since these three phases are the only ones indicated by the X-ray analysis of the alloys, an expansion on cooling must indicate the formation of alpha from gamma, of alpha from epsilon, or of gamma from epsilon, while a contraction

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[5]Seikichi Satô. "Dilatometric Investigation of the A_3 and A_4 Transformations in Pure Iron," *Philosophical Magazine*, Vol. 1, Ser. 7, 1926, p. 996.

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[6]M. Gensamer, John F. Eckel, and Francis M. Walters, Jr., "The Alloys of Iron, Manganese, and Carbon. Part III. An X-ray Study of the Binary Iron-Manganese Alloys", TRANSACTIONS, American Society for Steel Treating, May, 1932, p. 599.

on cooling will indicate the formation of epsilon from alpha, epsilon from gamma, or gamma from alpha. The reverse should occur on heating. It is known that gamma is the phase stable at higher temperatures,[7] so there is reason to believe that of these possibilities, an expansion on cooling represents the gamma to alpha change, while a contraction on cooling means the gamma to epsilon change, with the reverse on heating.

Calculations of this type yield a most interesting point on the allotropy of iron. The side of the unit cell for gamma iron when calculated from the alpha to the gamma lattice change with each atom occupying a constant volume, and using lattice dimensions corrected for thermal expansion by the application of the dilatometric data, yields a lattice dimension of 3.646 Å for gamma iron. (The volume of the elementary parallelopiped for the alpha phase is $\frac{a^3}{2}$, and for the gamma phase is $\frac{a^3}{4}$, since there are respectively two and four atoms in the unit cell. Then, if this volume is to remain constant $\frac{a_\alpha^3}{2} = \frac{a_\gamma^3}{4}$, or $a_\gamma = \sqrt[3]{2}.a_\alpha$. a_α corrected for thermal expansion is 2.894 Å at 900 degrees Cent. (1650 degrees Fahr.), so $a_\gamma = 1.26 \times 2.894 = 3.646$ Å). Now, if the least interatomic distance remained unchanged during this transformation, the lattice dimension should be 3.545 Å (the least interatomic distance for the gamma phase is $\frac{a}{\sqrt{2}}$, and for the alpha phase is $\frac{\sqrt{3}}{2}.a$, so $a_\gamma = \sqrt{\frac{3}{2}}.a_\alpha$). The contraction on this latter basis should be 0.101 Å or 2.8 per cent. Since the observed contraction is only 0.3 per cent, the actual lattice dimension for the gamma phase is 3.635 Å ($3.646 \times (1 - 0.003)$). From this, the least interatomic distance for the gamma phase is 2.57 Å ($d_\gamma = 3.635.\frac{\sqrt{2}}{2}$) and for the alpha phase, this distance is 2.51 Å ($d_\alpha = 2.894.\frac{\sqrt{3}}{2}$). Then the change from alpha to gamma is ac-

[7] Einar Öhman, "Röntgenographische Untersuchungen über das System Eisen-Mangan", Zeitschrift für Physikalische Chemie, Abt. B, Vol. 8, 1930, p. 81.

companied by an increase in the least interatomic distance of 0.06 Å, in spite of the observed decrease in volume. This may mean an actual expansion of the iron atom during the allotropic change, with the change in crystallographic type accommodating the increase with a minimum expenditure of energy.

A similar calculation made on the gamma to epsilon change, but without the advantage of knowing the thermal expansion of the epsilon phase, since it has never been positively observed alone, shows that the change is accompanied by a decrease in the least interatomic distance of 0.026 Å ($a_\gamma = 3.581$ Å, so $d_\gamma = 0.7071 \times 3.581 = 2.532$ Å; $a_\epsilon = 2.526$ and $c/a = 1.613$, so $d_\epsilon = a\sqrt{1/3 + 1/4\ (c/a)^2} = 2.506$ Å). This contraction cannot be checked dilatometrically, since the contraction calculated on the constant atomic volume basis yields a change of 0.68 per cent (see preceding paragraph) as opposed to an observed change of 0.25 per cent; this must mean that the changes from gamma to epsilon and from gamma or epsilon to alpha are occurring simultaneously, or in close sequence, or that the gamma to epsilon change is incomplete for this alloy. With X-ray data sufficiently accurate, it would be possible to calculate the relative amounts of the phases present.

Apparatus

In the design of a dilatometer, there are several requirements which it is desirable to meet as far as possible. The dilatometer should be usable from 900 degrees Cent. (1650 degrees Fahr.) or higher, to well below room temperature. Transformations of some iron alloys occur at the upper temperature, and then other transformations are by no means complete at room temperature. The device for indicating length or volume changes should permit quick and easy reading and should be capable of following rapid changes. It is desirable that the materials of which the dilatometer is constructed do not necessitate the introduction of corrections in order to obtain the true length change. In the case of the iron-manganese system, it is necessary to protect the alloys from oxidation. The specimen should be uniform in temperature throughout its length.

Many methods have been used in the observation of thermal expansion. Each method, however, has its particular disadvantage. The micrometer microscope gives definite results but the time required to make observations limits its usefulness in following rapid changes in

length. The optical lever offers certain mechanical difficulties in its design. The great sensitivity of the interferometer, which permits the use of small samples, makes its use desirable when possible. The highest temperature at which it may be used for metals is about 500 degrees Cent. (930 degrees Fahr.), which is one reason why it was not adopted for this investigation. Various electrical methods have been used, such as the measurement of changes in the inductance of

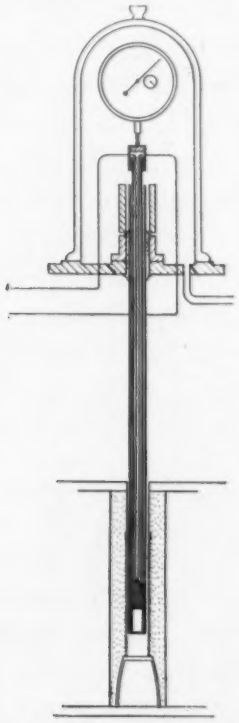

Fig. 1—Section of Dilatometer.

a magnetic circuit in which some element of the circuit is moved relative to some other element or the change in capacity of two plates whose distance apart is influenced by the dilatation of the specimen. These methods have the disadvantage of requiring calculation to change the observed readings to changes in length. The dial gage has the advantage of being direct-reading, and readily set up. While it lacks the highest precision, it covers a fairly large range with a high degree of sensitivity.

The dilatometer used (Fig. 1) is a modification of one described by the Bureau of Standards.[8] It consists, essentially, of a trans-

[8]Peter Hidnert and W. T. Sweeney, "Thermal Expansion of Magnesium and Some of Its Alloys", Bureau of Standards Journal of Research, Vol. 1, 1928, p. 771.

parent quartz tube, 18 inches long, sealed at the lower end by a flat quartz plate. On the bottom of the quartz tube is a one inch length of quartz tubing, upon which the specimen, one-inch long, rests. On top of the specimen is another quartz tube which transmits the dilatation of the specimen to a dial gage. The gage has a total movement of 0.1 inch, for which the pointer makes ten revolutions. The dial is connected by the lug on the back to the outside quartz tube by the device described by the Bureau of Standards. This assembly is cemented in a hole in the brass plate upon which the bell jar is placed. Two forms of specimen have been used, one a solid and the

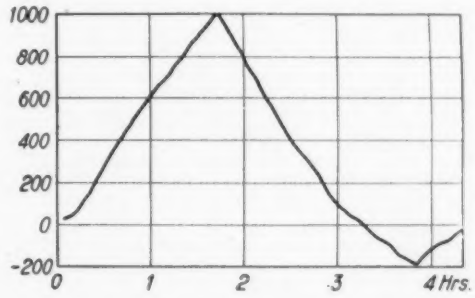

Fig. 2—Time-temperature Diagram, Showing Normal Rate of Heating and Cooling.

other a hollow cylinder. Both ends of the solid cylinders were turned to a slightly smaller diameter, so as to fit inside the quartz tubes at the top and bottom and insure centering. In the case of the hollow cylinder, the diameter was decreased only at the lower end. The effective length of the specimen was one inch; its diameter in the largest part was approximately one-half inch. The thermocouple was attached directly to the sample by pounding the thermocouple bead into a saw cut in the upper end of the sample. The thermocouple wires were run through a two-hole refractory tubing. They were led through the brass plate and sealed with a vacuum gutta-percha cement which served also as electrical insulation. The furnace winding of alloy resistance wire was five inches long. Only enough refractory was used outside of the winding to hold it together; consequently, the furnace was very responsive to changes in power input. The furnace was placed around the specimen so that the specimen was at the center of the winding. The thermocouple used was chromel-constantan and was calibrated below room temperature by direct immersion in liquid nitrogen and by comparison with a petane in glass ther-

mometer; above room temperature, the calibration of the maker was used.

In observing dilatation, the current was started at two amperes and increased at the rate of 0.1 ampere every two minutes until a maximum of about seven amperes was reached. On cooling, the current was decreased at the rate of 0.2 ampere per minute.

Fig. 3—Dilatation of Binary Iron-Manganese Alloys.

The furnace was dropped when the temperature had fallen to 200 degrees Cent. and, when room temperature was reached, a Dewar flask, containing liquid nitrogen, was raised in steps until the minimum temperature was reached. (See Fig. 2). In some cases, twice as rapid heating and cooling rates were used, particularly at high temperatures where there was evidence of creep. The low manganese alloys were observed in vacuo. An atmosphere of helium was used for

the higher manganese alloys and for those runs in which the temperature was held over night or longer. In the results presented in this paper, no correction has been made for the dilatation of the quartz.

Results[9]

The specimen used for the dilatation curve labeled 0 per cent manganese, Fig. 3, was vacuum-melted electrolytic iron containing 0.012 per cent carbon. The hysteresis at the A_3 point, we believe to be due to the rapid rate of heating and cooling employed, since with even the usual rate, the specimen decreased in length about 0.1 per cent at this temperature.[10] This was due, probably, to the plasticity of iron at the A_3 point as demonstrated by Professor Sauveur.[11] A minute change in slope at about 750 degrees Cent. (1380 degrees Fahr.) may be the A_2 point, although the change actually observed is of the same order of magnitude as that due to a sudden change in heating rate. The change in slope on heating at 400 degrees Cent. (750 degrees Fahr.) may be due to carbon, since saturation may be expected at about this temperature for the percentage of carbon in the iron used. The second curve for this alloy shows that this change in slope is present even if the sample is not carried through the alpha-gamma transformation. The 1.1 per cent manganese alloy shows much the same features as the alloy without manganese, but the alpha to gamma transformation begins at a lower temperature, and the reverse transformation is still further depressed.

The curve given for the 4.4 per cent manganese alloy shows a failure to close, which is sometimes observed. This may be due to the specimen securing a better seat sometime during the run. The lack of closure shown here amounts to 0.0004 of an inch. In the 4 and 7 per cent alloys, the coefficient of expansion of the alpha phase is definitely less than that of the gamma phase. If the alloys are heated and cooled between the transformations, there is no departure from the curves.

In the case of the 10 per cent alloy, Fig. 4, it is obvious that not

[9]Compare Alfred Schulze, "Über die thermische Ausdehnung von Eisenlegierungen", *Zeitschrift für Technische Physik*, Vol. 9, 1928, p. 338.
Also, Torajirô Ishiwara, "On the Equilibrium Diagrams of the Aluminum-Manganese, Copper-Manganese and Iron-Manganese Systems." *Science Reports*, Tohoku Imperial University, Vol. 19, 1930, p. 499.

[10]Compare Wilmer Souder and Peter Hidnert, "Thermal Expansion of Nickel, Monel Metal, Stellite, Stainless Steel, and Aluminum", United States Bureau of Standards Scientific Papers, Vol. 17, 1922, p. 497.

[11]Albert Sauveur, The Metallography and Heat Treatment of Iron and Steel, Third Edition, 1926, p. 108.

only has the critical range been lowered, but also the heating curve has become approximately parallel to the cooling curve. On subsequent heatings to temperatures below the alpha to gamma transformation, the slope approaches that of alpha iron and the curves close

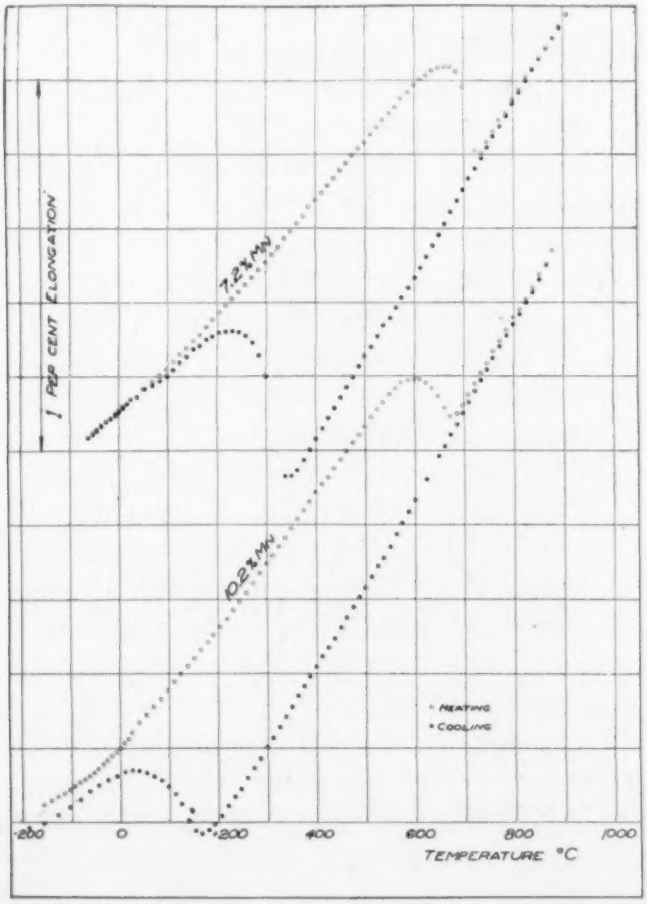

Fig. 4—Dilatation of Binary Iron-Manganese Alloys. Observations, for These Alloys As Well As for the Others, Were Made at One Millivolt Intervals.

on completing the cycle. With this composition, there is evidence of the appearance of a third phase.

That a third phase is present, however, becomes more definite from the observations on the 13 per cent alloy (Fig. 5). Starting at room temperature, (a), this alloy undergoes a sudden expansion, (b), starting about 200 degrees Cent.; then expands at a uniform rate until a temperature of 570 degrees Cent. is reached, when it undergoes a contraction, (c). That this contraction is alpha to gamma is indicated by the fact that the temperature is that which might be

expected from the rate at which the temperature of this transformation is lowered with increasing manganese content. On cooling, this alloy decreases in length at about the same rate as the alloys of lower manganese content until the temperature of 150 degrees Cent. is reached, when it undergoes a definite contraction, (d). This con-

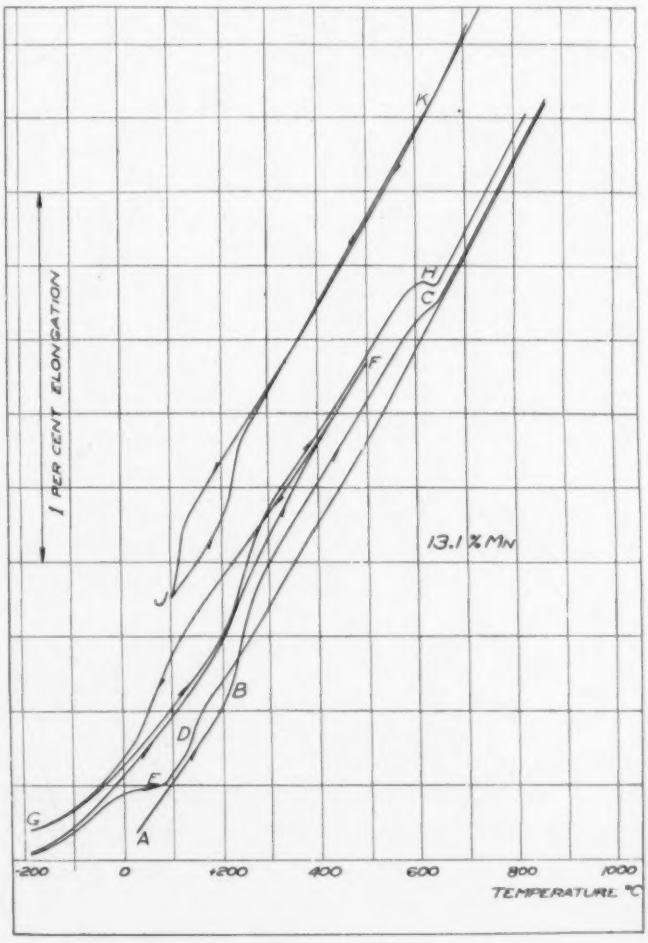

Fig. 5—Dilatation of 13 Per Cent Iron-Manganese Alloy.

traction indicates that at this temperature, there is a change from gamma to epsilon, since epsilon has a smaller specific volume than gamma. The transformation to epsilon is evidently incomplete, since the decrease in length to be expected from X-ray data is 0.68 per cent; the greatest decrease observed was 0.25 per cent. If the alloy is slowly cooled from 100 degrees Cent. to room temperature, as is the case here, a definite expansion occurs a little below 100 degrees Cent.,

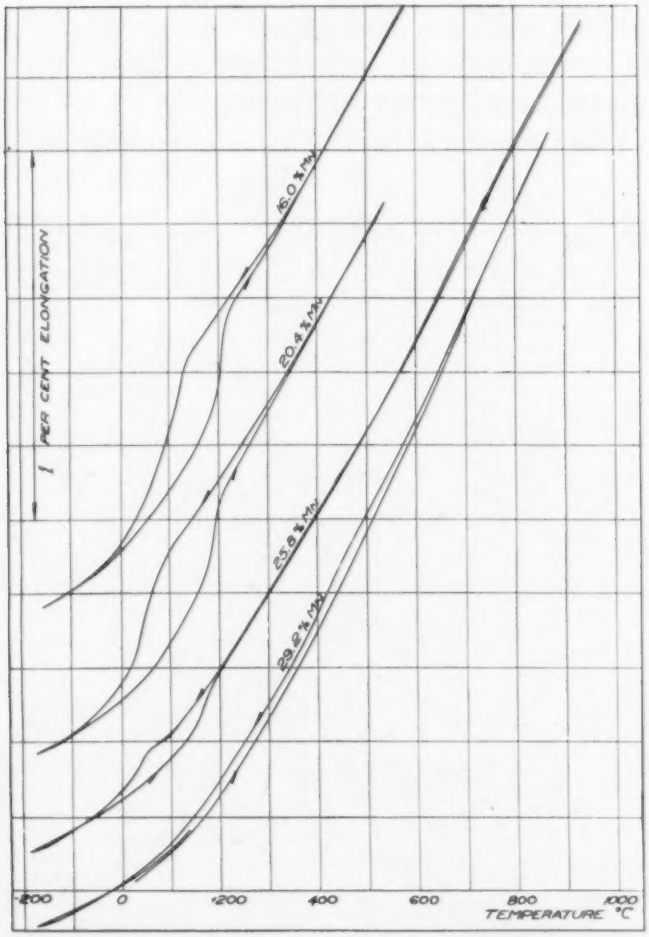

Fig. 6—Dilatation of Binary Iron-Manganese Alloys.

(e). This is believed to be the transformation from gamma to alpha. Since this phase change is an expansion, it can also be due to a transformation from epsilon to alpha. That it is not epsilon to alpha is shown in two ways:

(1) When the alloy was heated to 500 degrees Cent., (f), and then was returned to liquid air temperature, (g), the loop thus formed indicates that that part of the gamma which had been transformed into epsilon on cooling changed back to gamma between 200 and 400 degrees Cent. On heating the alloy to 600 degrees Cent., the alpha to gamma transformation is again obtained, (h).

(2) If, however, the alloy is permitted to cool only to 100 degrees Cent., and even if held at this temperature seventeen

hours, as it was in the case of the curve shown at (j), no evidence will be found for the alpha to gamma transformation on heating through the range in which this transformation is ordinarily observed, (k).

It is concluded from the runs shown in Fig. 5, as well as many others on this alloy, that the epsilon phase, after its formation on cooling, remains relatively stable and changes back into gamma on heating to

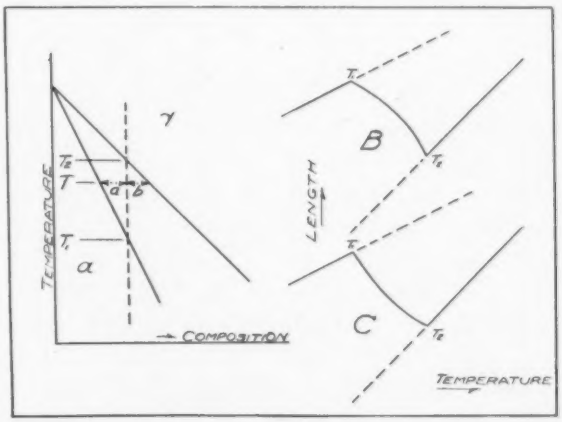

Fig. 7—"B" is the Theoretical Dilatation Curve for the Phase Diagram Shown; "C," for the Phase Boundary Lines More Nearly Parallel.

about 200 degrees Cent. and that the alpha phase which appears is formed at the expense of the gamma iron.

The 16, 20, and 26 per cent manganese alloys (Fig. 6) show a progressive lowering of the epsilon-gamma transformation points, a smaller percentage of epsilon formed, and no definite indication (from dilatometric observations) of the formation of the alpha phase. The 29 per cent alloy shows no hysteresis loop, but the marked change in slope near room temperature agrees with the X-ray data, indicating that some epsilon is still formed.

The great difference in temperature between the transformation on heating and the transformation on cooling in the 4 per cent and 7 per cent alloys is usually ascribed to "sluggishness." Accordingly, in the case of the 7 per cent alloy, an attempt was made to determine the rate of transformation of gamma to alpha at temperatures higher than that at which the transformation occurred at the relatively rapid cooling rate used for the observations. Holding this alloy, however, at 630 degrees Cent. (1165 degrees Fahr.) for seventeen hours and at 400 degrees Cent. (750 degrees Fahr.) for forty-one hours pro-

duced no observable transformation of gamma to alpha. It was found, however, that varying the rate of temperature change on passing through a phase change does have a marked effect on the rate of change of length.

Effect of Heating Rate

To determine the manner in which the length may be expected to change on going through a transformation occurring over a considerable temperature range, certain simple assumptions may be made.

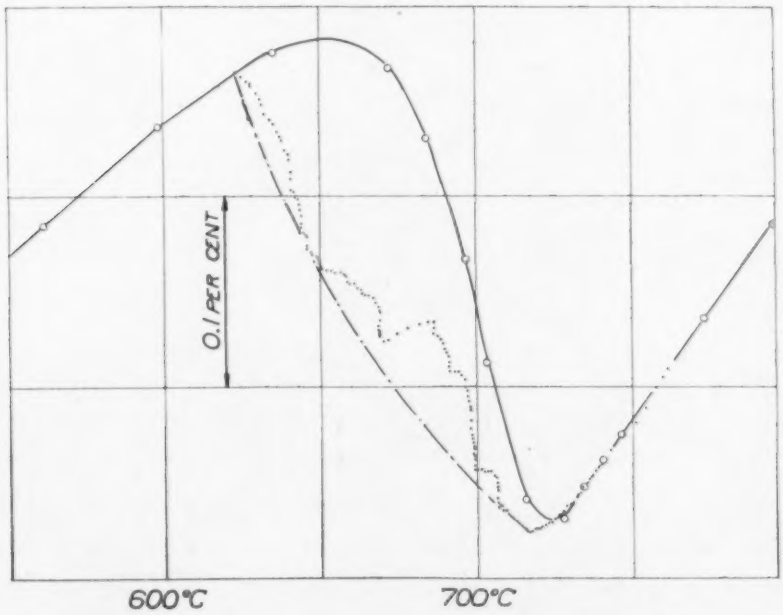

Fig. 8—A Two and One-Half-Hour Heating Through the Alpha-Gamma Range of the Seven Per Cent Alloy Compared with a Six-Minute Heating.

Curve "B," Fig. 7, has been obtained graphically by reasoning that the fractional change which has taken place at the temperature T on heating is given by the ratio $\frac{a}{a+b}$ in the equilibrium diagram, Fig. 7; and that the length of the specimen will be divided in this ratio between the length for each phase alone when the thermal expansion curves are extrapolated to the temperature T. The same curve results on cooling. As the phase boundary lines in the equilibrium diagram become more nearly parallel, the curve assumes the shape of "C," Fig. 7. Similar curves are expected if the phase boundary lines are curved.

To test these conclusions, the 7 per cent alloy was taken through

the alpha-gamma transformation as slowly as could be managed with the means of temperature control available. In Fig. 8, observations of the usual rate of heating are shown by the smooth curve, circles indicating observations approximately one minute apart. The observations for the slow rate of heating were made one minute apart and are indicated by dots. As the heating rate became slow enough to approach "equilibrium," the observations appeared to approach the curve indicated by the dashed line, which is similar to the theoretical curve.

DISCUSSION

Written Discussion: By N. A. Ziegler, research laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh.

Dr. Walters and his co-workers should be congratulated for an excellent piece of research. The writer from personal experience knows most of the difficulties which are met in vacuum-metallurgical work.

With the equipment which is at Dr. Walters' disposal the design and operation of vacuum furnaces described by him is an interesting solution of the problem.

I, however, believe that the best type of laboratory high frequency vacuum furnace is one described by Mr. Brace and myself,[1] i. e., "the high frequency vacuum furnace of bell jar type." The following are relative advantages of the "bell jar" furnace:

1. All flexible and wax joints are eliminated, which makes control of vacuum and elimination of possible leaks much easier.

2. Larger charges in a higher vacuum can be melted. In the furnace just mentioned, 12 pounds of electrolytic iron can be melted and maintained in molten state for an indefinite period of time in a vacuum of 0.001 millimeters of mercury or better.

3. Charging and cleaning of a bell jar furnace is much easier. In the furnace described by Dr. Walters it is necessary to manipulate in a long and narrow space.

4. The danger of a crucible breaking and molten charge running out is less, because the crucible is supported by a flexible water-cooled copper helix (which also acts as the heating element).

However, a considerable drawback of a bell jar furnace is that, due to the fact that the high frequency coil is in vacuum, it is restricted to relatively low frequencies and voltages, obtainable only from a high frequency generator. With an Ajax-Northrup mercury gap oscillator, which is used by Dr. Walters as a source of power, very high voltages are developed. For this reason the heating coil cannot be placed in vacuum on account of severe sparking being developed, and danger of ruining the furnace.

[1] P. H. Brace and N. A. Ziegler, "A High Vacuum Induction Furnace, and its Application to the Study of Gases in Metals," *Proceedings*, Institute of Metals Division of American Institute of Mining and Metallurgical Engineers, 1928, p. 594.

Hence, I once more wish to express my admiration of the excellent vacuum furnaces which Dr. Walters and his colleagues succeeded in constructing.

Written Discussion: By F. T. Sisco, editor, Alloys of Iron Research, Engineering Foundation, New York City.

It seems hardly necessary to comment on the quality of the work by Dr. Walters and his associates as outlined in these four papers, or to call attention to its importance. Surely no ferrous alloys rank higher in importance than those of the binary iron-manganese or the ternary iron-manganese-carbon systems. Hadfield's original research on 14 per cent manganese steel was reported more than 40 years ago and a large amount of work has been done on commercial manganese steel in the interim, but in spite of this we have little reliable information on the constitution of the pure ternary alloys. Even the binary system has received scant attention. This will be evident if the results by Walters and his associates are compared with work done in the past. Even the equilibrium diagram in the International Critical Tables (Vol. II, p. 450) represents information far from the truth.

The effect of extremely small amounts of solid and gaseous impurities on the properties of pure metals is only now being fully appreciated. Much of the past research work on binary and ternary iron alloy systems is wholly, or at least partially, invalidated because the investigator did not pay sufficient attention to the effect of accidental or unavoidable impurity. It is gratifying to note that Dr. Walters and his associates have used great care in the preparation of their alloys, and have apparently considered every variable which might affect the accuracy of the results.

This investigation on the binary alloys, and work now in progress on the ternary alloys should be of marked value in clarifying our knowledge of the iron-manganese system. It is unfortunate that the authors have not presented a tentative equilibrium diagram of the binary alloys. It is hoped that this will be forthcoming soon.

Written Discussion: By Marcus A. Grossmann, Illinois Steel Company, Chicago.

Dr. Walters has rendered a distinct service in organizing and carrying out these researches on alloys of iron and manganese. The distillation of the manganese in vacuum is a warrant for the purity of the alloys studied. His Figs. 5 and 6 on page 595, indicating the critical points, give a clear picture of the positions and intensities of the transformations in the alloys up to about 20 per cent manganese. His Fig. 8 on page 597 and the discussion of the transformation points in the alloy with 13 per cent manganese, will be particularly interesting in further study of Hadfield manganese steel, especially also in connection with Mr. Scott's dilatation studies. We look forward to a continuation of these studies to include appreciable carbon contents.

Authors' Closure

We wish to thank those who have discussed our papers for their kind comments.

In regard to the advantages of the bell jar vacuum furnace Mr. Ziegler neglected to point out that better coupling between the coil and the charge is

secured in his furnace. We have used our furnace two years without an accident. In the distillation of manganese, the pressure drops to 0.001 millimeters toward the end of the run. In melting electrolytic iron, we stop when the pressure falls to 0.01 millimeters, because at this pressure the carbon is usually down to the desired limit, 0.01 per cent. Our furnace does not involve the use of copper-glass seals and can be constructed by any mechanic for about a hundred dollars.

We have not presented even a tentative equilibrium diagram at this time because further studies of the alloys are in progress; a redetermination of the solidus-liquidus, thermomagnetic analysis, the variation of electrical conductivity with temperature, further X-ray studies, and the effect of cold work upon the transformations.

IMPACT CHARACTERISTICS OF STEEL RAILS AT LOW TEMPERATURES

By J. F. Cunningham and James Gilchrist

Abstract

In the pearlitic rail steels tested, a reduction in impact resistance was found to occur gradually down to temperatures of —18 to —20 degrees Fahr. From that temperature down, the resistance to shock has reversals at fairly definite temperatures. Tests were also made on carbon steels containing 0.10, 0.42 and 0.92 per cent carbon and also open-hearth iron. With the exception of the 0.10 per cent carbon rivet steel all the materials show this definite change in impact values at similar temperatures. The 0.10 per cent carbon rivet steel does not show similar reversals but gradually loses resistance to shock after a temperature of —40 degrees Fahr. is passed. Conclusions are drawn that the different components (cementite, ferrite, etc.) may have different coefficients of contraction due to temperature change, and cause minute strains in the structure, fully developed at or near —18 to —20 degrees Fahr. Also that these coefficients may be constant down to a temperature of —18 to —20 degrees Fahr. but not below that temperature.

DURING the winter of 1929-1930 Canadian railway companies suffered severe losses from rail fractures, the fractures occurring mainly in the very cold belts in sub-zero temperatures. Investigation showed that the failures were not caused by fissures in the metal and as no data were available on the effect of low temperatures on steel rails the authors outlined a series of laboratory tests to determine the effects of low temperatures on impact resistance of rail sections. Some work has been done in this field by Sir Robert Hadfield, Professor Kammerlingh Onnes and Sir Edward Dewar who were however interested in physical rather than mechanical changes

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A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. Of the authors who are members of the society, J. F. Cunningham is superintendent and engineer of tests at the engineering testing laboratories, University of Manitoba, Winnipeg, Canada, and James Gilchrist is steel supervisor and chief inspector of materials, Canadian National Railways, Winnipeg, Canada. Manuscript received April 24, 1931.

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Procedure of Investigation

Two series of experiments were conducted. The test pieces used in the first series were made from steel rails furnished by the Canadian National Railways, one a new rail, the others having been in service for a number of years. For the second series of tests, billets of open-hearth iron and of steels containing 0.10, 0.42 and 0.92 per cent carbon were provided.

From the rails, specimens ½ inch square and 16 inches long were machined. The specimens were taken from five sections of each rail, namely, the web, the gage side of the head, the outside of the head, the gage side of the base and the outside of the base. The specimens were carefully shaped to standard Izod test pieces sized to a special steel gage block and tested in an Izod 100 foot-pound single-blow impact machine. The test pieces were cooled to the desired temperature with acetone and dry ice (solid CO_2) kept in a silvered Dewar flask. The temperatures were measured with a spirit thermometer graduated in degrees Cent. The test pieces were raised

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[4] Guillet and Revillon, *Revue de Metallurgie*, Vol. 6, 1909, p. 94-101 and 918-924.

[5] Mr. Yamada, *Science Reports*, Tohoku Imperial University (1) 15, No. 5, 1926.

[6] "Impact Resistance of Steels at Low Temperatures," by Cameron, paper read to Empire Mining and Metallurgical Congress, Edmonton, Alberta, Canada, 1927.

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and lowered through the solution by means of an attached thread, and the temperature brought to the desired point after immersion. In this way it was thought that more accurate results could be obtained than by allowing the cold solution to be raised from extremely low temperatures by the immersion of the warm test pieces. Also a more uniform temperature throughout the section of the test piece could

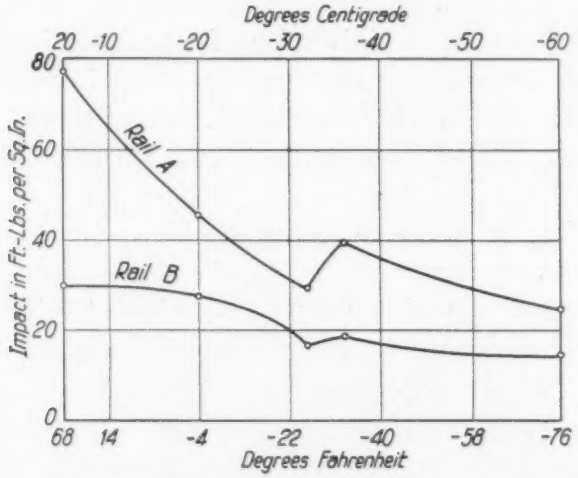

Fig. 1—Effect of Low Temperature on Impact Properties of Rails A and B. Curves Plotted from Average Values of Five Specimens.

be obtained by this means. The size of the Dewar flask available was such that only three specimens could be cooled at one time. In order to measure the temperature gradient in moving the specimens to the vise of the testing machine, a dummy test piece was made which had a hole for the thermometer in the center. It was found that except at very low temperatures the rise in temperature in transferring the test piece from the cooling medium to the testing machine was negligible. A further precaution was taken by cooling the machine vise with CO_2 snow in the summer and by keeping the laboratory windows open in the cold winter months.

The results obtained are indicated in the tables and charts. Table I contains the impact values obtained from testing two sets of test pieces from the rails. The test pieces were broken at five temperatures: 20, —20, —32, —36 and —60 degrees Cent. (68, —4, —26, —33 and —76 degrees Fahr.). It was noted that the impact values decreased as the temperature of the pieces was lowered from 20 to —32 degrees Cent. (68 to —25 degrees Fahr.) and that a further lowering of the temperature to —36 degrees Cent. (—33 de-

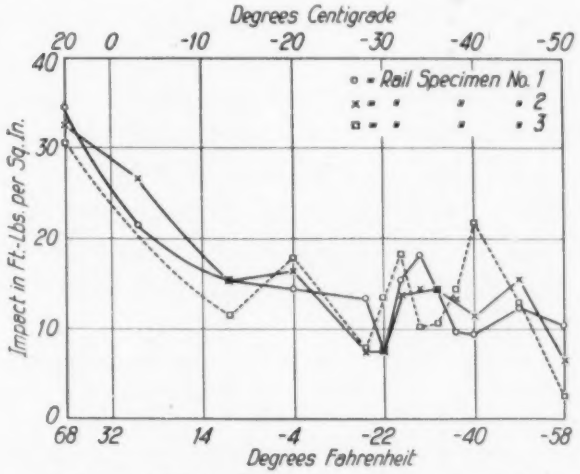

Fig. 2—Effect of Low Temperature on Impact Properties of Rail Specimens No. 1, 2 and 3. Curves Plotted from Average Values of Four Test Specimens for each Temperature.

grees Fahr.) was accompanied in nearly every case by a corresponding rise in impact values. The conclusion appears to be that there is a definite reversal in the impact values of steel rails around a temperature of —32 degrees Cent. (—26 degrees Fahr.). In the table the test pieces marked A_1, A_2, etc., are from one of the used rails, those marked B_1, B_2, etc., are from the new rail. Each number in the table is the average of two tests. Fig. 1 shows average impact values of the two rails A and B. The upper curve is plotted from the average values of the five "A" specimens recorded in Table I;

Table I

Impact Value in Ft.-Lbs. Per Square Inch at Various Temperatures of Two Rail Steels

Specimen	20° C. 68° F.	—20° C. — 4° F.	—32° C. —20° F.	—36° C. —32° F.	—60° C. —76° F.	% Increase in Impact Resistance Between —20 and —35° F.
A_1 Gage side	59.5	55.0	31.8	38.6	23.2	+24.4
A_2 Outer side	69.7	38.5	23.6	46.3	23.5	+96.3
A_3 Web.	67.3	31.1	23.4	33.8	15.5	+43.6
A_4 Outer base	69.1	45.1	33.8	44.6	18.6	+24.2
A_5 Gage base	110.5	55.8	32.8	32.5	42.2	— 1.54
B_1 Gage side	88.8	57.6	20.7	21.6	14.3	+ 4.34
B_2 Outer side	16.4	12.3	16.7	16.2	14.3	— 3.08
B_3 Web.	15.3	15.8	14.2	16.0	14.3	+11.3
B_4 Gage base	24.4	16.3	16.4	21.9	14.2	+33.5
B_5 Outer base	24.3	15.5	14.6	16.3	14.8	+11.6

the lower curve the average values of the five "B" specimens. Thus each point plotted represents the average value of ten test pieces.

In order to study this phenomenon more completely 400 test pieces were machined from rails C and D, and tested at increments of 2 degrees Cent. between —28 to —40 degrees Cent. (—18 to —40 degrees Fahr.), that being the range of paramount interest. Test pieces No. 1, 2 and No. 3 were made from the base, head and web respectively of rail "C" No. 4, No. 5 and No. 6 from the corresponding portions of rail "D."

The chemical compositions of the six groups are as follows:

Rail "C"	No. 1—Base Per Cent	No. 2—Head Per Cent	No. 3—Web Per Cent
Carbon	0.60	0.57	0.60
Manganese	0.75	0.76	0.76
Phosphorus	0.055	0.050	0.050
Sulphur	0.032	0.030	0.030

Rail "D"	No. 4—Base Per Cent	No. 5—Head Per Cent	No. 6—Web Per Cent
Carbon	0.62	0.62	0.60
Manganese	0.72	0.72	0.72
Phosphorus	0.022	0.020	0.020
Sulphur	0.029	0.030	0.030

The results are shown in Fig. 2 and Fig. 3 which are plotted

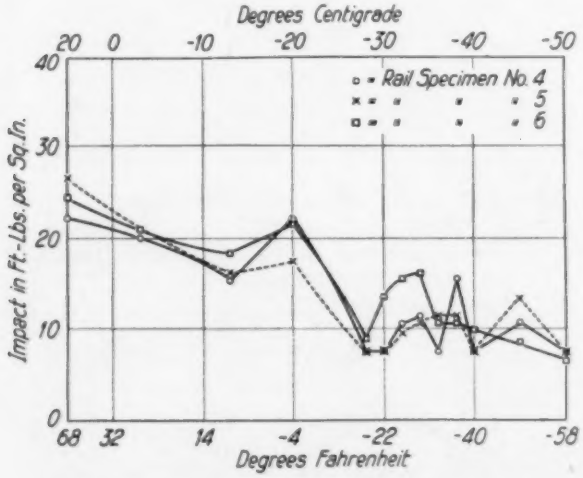

Fig. 3—Effect of Low Temperature on Impact Properties of Rail Specimens No. 4, 5 and 6. Curves Plotted from Average Values of Four Test Specimens for each Temperature.

from the average impact value of four test pieces for each point of the curves. Indications of reversal of impact values are to be seen at temperatures from —28 to —30 degrees Cent. (—18 to —22 degrees Fahr.). In this connection it is interesting to note that in the

Table II

Showing the Variation Between the Maximum and Minimum Values for Each Set of Four Specimens Which Were Averaged for Points on the Curves.

Figures given in foot-pounds per square inch

Temp. Deg. Cent.	−3	−13	−20	−28	−30	−32	−34	−36	−38	−40	−45	−50
Temp. Deg. Fahr	26.6	8.6	−4	−18.4	−22	−25.6	−29.2	−32.8	−36.4	−40	−49	−58
Rail 1	0	0	1.91	0	0	0	5.72	5.72	0	3.82	1.91	0
Rail 2	3.43	0	1.91	0.76	0	3.05	1.91	5.72	3.82	0.76	3.82	1.91
Rail 3	....	0	0.76	0	5.72	5.72	1.14	1.53	5.72	3.82	5.72	4.58
Rail 4	1.91	0	3.80	0	0	5.72	2.67	0	0	0	1.53	0
Rail 5	....	.	....	0	0	0	2.67	3.82	3.82	0	0	0
Rail 6	0	0	0	1.91	0.91	0	1.91	1.91	3.82	3.05	1.91	1.91

The maximum difference.....5.72 foot-pounds per square inch

most recent paper by F. Sauerwald and K. A. Pohle[8] mention is made of both brittle and ductile breaks occurring in iron at various temperatures between −180 and −90 degrees Cent. (−292 and −130 degrees Fahr.) especially in two-crystal systems. Fig. 4, Fig. 5 and Fig. 6 show representative structures containing minimum, mean and maximum amounts of excess ferrite in the six groups mentioned above. In Table II are shown the differences in maximum and minimum impact values averaged for each set tested, the greatest value being 5.72 foot-pounds per square inch.

The nature of the materials used in the second series of tests is shown in the following tabulation:

	Special Steel Per Cent	Intermediate Steel Per Cent	Rivet Steel Per Cent	Open-Hearth Iron Per Cent
Carbon	0.92	0.42	0.10	0.02
Manganese	0.68	0.58	0.40	....
Phosphorus	0.036	0.021	0.018	....
Sulphur	0.055	0.035	0.036	....

Test pieces similar to those in the first series were prepared and the same methods of testing employed. The results shown in Fig. 8 indicate a similar behavior to that observed in steel rails. A definite reversal of impact resistance occurs in the vicinity of −35 degrees Cent. (−30 degrees Fahr.). Each point on the curves represents an average of four tests. The tests on 0.10 per cent rivet steel, the results for which are shown in Fig. 9, reveal that there is no reversal of impact resistance. Instead there is manifested a high resistance to impact until a temperature of −40 degrees Cent. (−40 degrees Fahr.) is reached after which there is a gradual decrease in impact resistance.

[8] "Ueber den Bruchvorgang in Eisen bei tiefen Temperature," by K. A. Pohle, *Zeitschrift für Physik*, Vol. 56, 1929, Nos. 7 and 8, p. 576-578. Also *Zeitschrift für Physik*, Vol. 67, January 1931, Nos. 3 and 4, p. 179-183.

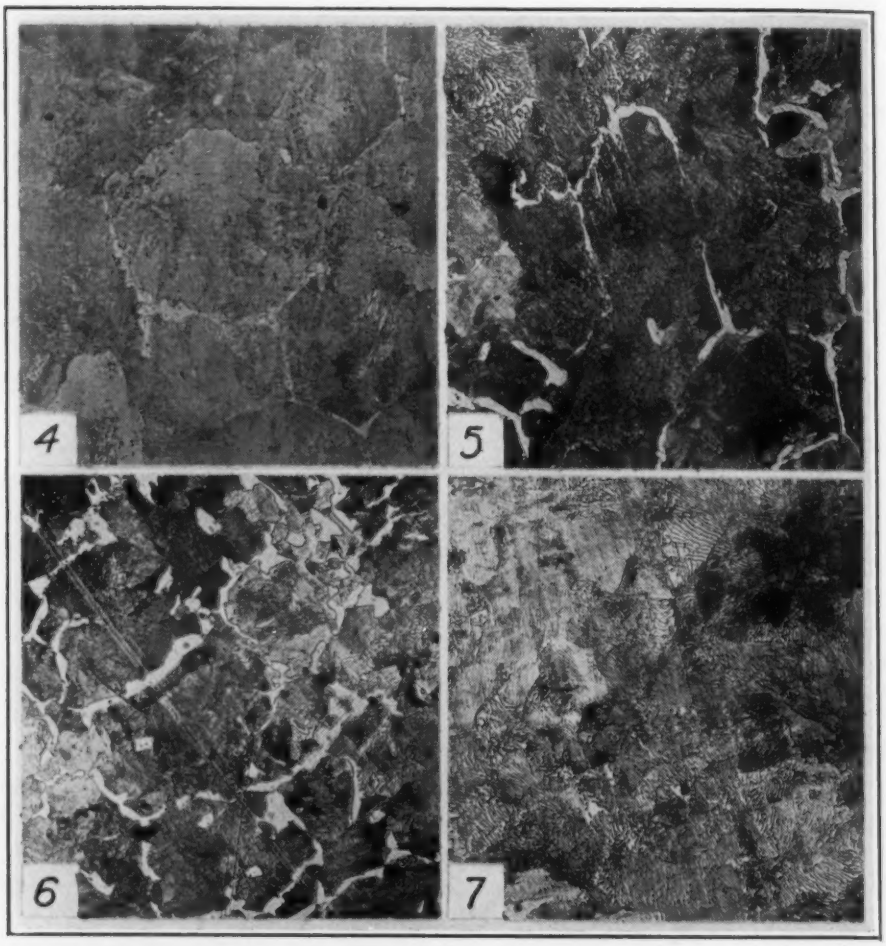

Fig. 4—Photomicrograph of Rail No. 6. Taken from the Web Section.
Fig. 5—Photomicrograph of Rail No. 2. Taken from the Head Section.
Fig. 6—Photomicrograph of Rail No. 1. Taken from the Base Section.
Fig. 7—Photomicrograph of 0.92 Per Cent Carbon Steel. All Specimens Etched in 2 Per Cent Nital. Specimens Figs. 4, 5 and 6. × 175. Fig. 7—× 350.

At —70 degrees Cent. (—94 degrees Fahr.) which is the lowest temperature at which tests were made the resistance to impact is less than one-third of the value at —40 degrees Fahr. At no point in this range of temperature is there any indication of reversal of resistance to impact.

Discussion

A study of the fractured edges appears to reveal that the fractures in rail steel follow through the large pearlite grains and follow the contour of the lamellæ at the temperature of —29 degrees Cent. (—20 degrees Fahr.). At the lower temperatures the fracture is in-

dependent of the structure of the metal and the metal breaks without any apparent deformation. The specimens tested at the higher ranges of temperature show a distortion due to elongation at the edges. This is more easily illustrated by the 0.10 per cent carbon rivet steel Fig.

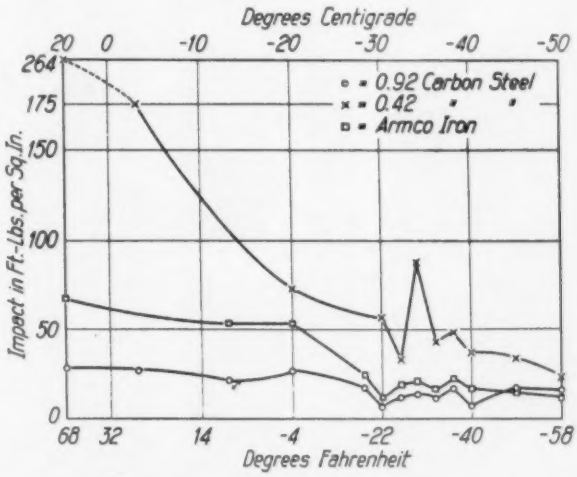

Fig. 8—Effect of Low Temperatures on Impact Properties of Open-hearth Iron, 0.92 and 0.42 Per Cent Carbon Steels. Curves Plotted from Average Values of Four Test Specimens.

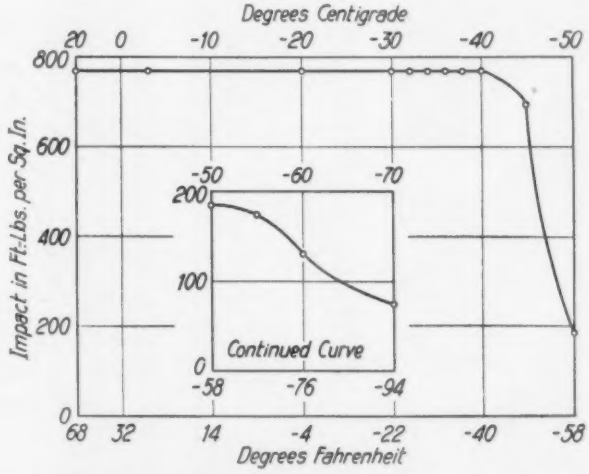

Fig. 9—Effect of Low Temperatures on Impact Properties of Rivet Steel—0.10 Per Cent Carbon.

10 where it can be noted that the necking gradually decreases as the temperature is reduced down to —40 degrees Fahr. The fracture in the material is fibrous in appearance down to a temperature of —34 degrees Cent. (—29 degrees Fahr.) and gets gradually more crystalline in appearance until at —40 degrees Fahr. the whole fractured sur-

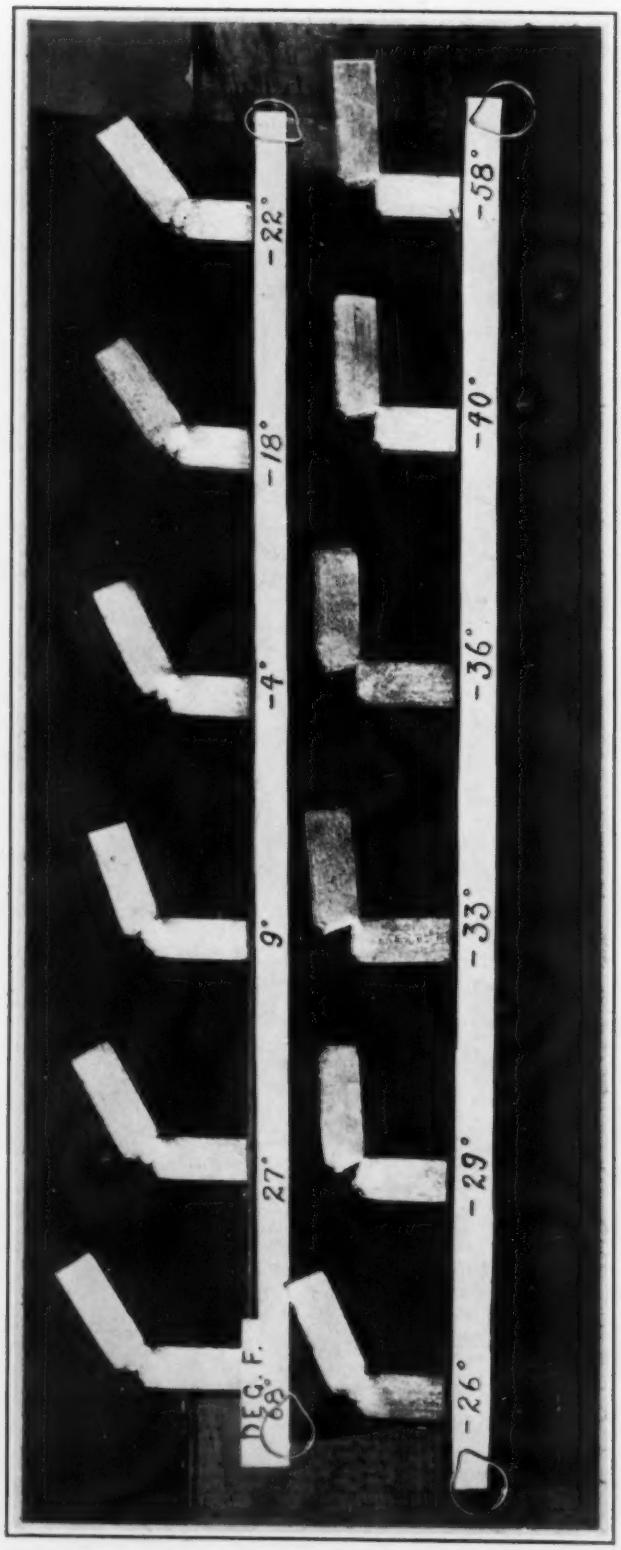

Fig. 10—Photograph of Rivet Steel Impact Tests at Various Temperatures. Necking Gradually Decreases as the Temperature is Reduced Down to —40 Degrees Fahr.

face becomes bright crystalline in appearance and the upper portion is completely severed in the test. Mention of this is made by F. Sauerwald and K. A. Pohle[8], who state that at normal temperatures the fracture is intracrystalline, but with decreasing temperatures down to —170 degrees Cent. (—274 degrees Fahr.) the fracture becomes intercrystalline.

The 0.92 per cent carbon steel compares in results with specimens No. 1 and No. 4. The microstructure of the 0.92 per cent carbon steel Fig. 7 is small-grained pearlite, and the results show a marked decrease in resistance to impact at —30 degrees Cent. (—22 degrees Fahr.) but do not reach that minimum value again down to —50 degrees Cent. (—58 degrees Fahr.).

Specimen No. 1 has an excess of ferrite surrounding fairly large polyhedral pearlitic grains* and the resistance to impact of this material shows a large decrease as soon as 32 degrees Fahr. is passed, but again the minimum resistance occurs at —22 degrees Fahr. It is not quite as large a decrease as that of the 0.92 per cent carbon steel, but in both materials this minimum value is not reached again down to a temperature of —50 degrees Cent. (—58 degrees Fahr.).

Specimen No. 4 is large-grained, fine pearlite* and little excess ferrite; the resistance of this material is the same at —28, —30, —40 and —50 degrees Cent. (—18, —22, —40 and —58 degrees Fahr.), but between each of these temperatures there is a distinct rise in impact resistance.

On comparing specimens No. 5 and No. 2, it was noted that the microstructures are quite similar, being large grains of medium pearlite* surrounded by a slight excess of ferrite. The minimum resistance to impact is reached in both these materials at —28 degrees Cent. (—18 degrees Fahr.) and the reversal of impact values in neither case is so marked as in the other steels. The actual results compare more nearly with those of open-hearth iron, although the normal temperature values are only about one-half those of open-hearth iron. This of course is due to the difference in ductility of the two materials. These two specimens were taken from the head of rails "C" and "D" and the results show that each part of the rail has similar characteristics at low temperatures, although the impact resistance values vary for different parts of the rails.

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*NOTE: As it appears under 175 diameters. Also ref., TRANSACTIONS, American Society for Steel Treating, O. V. Greene, "Some Characteristics of Pearlite in Eutectoid Rail Steels," Vol. XVI, July, 1929.

Comparing specimens No. 3 and No. 6, reversals still appear, No. 3 has large-grained medium pearlite* with quite an excess of ferrite. This specimen has a slight increase in the overall resistance to impact at lower temperatures.

Conclusions

1. In the specimens of rails tested, and in 0.92 per cent carbon, 0.42 per cent carbon steels and open-hearth iron, there is a gradual decrease in impact resistance down to temperatures of —28 to —29 degrees Cent. (—18 to —20 degrees Fahr.). From this point the resistance to impact has reversals at fairly definite temperatures.

2. Uncertain results may be expected in shock resistance below a temperature of —29 degrees Cent. (—20 degrees Fahr.).

3. The only material tested not showing these reversals is the 0.10 per cent carbon rivet steel which does not suffer from reduced temperatures until —40 degrees Fahr. is reached.

4. Ferrite grains from small to medium sizes will resist the lower temperature effects better than larger grains.

5. Medium grains of medium pearlite with a slight excess of ferrite are more resistant to impact at low temperatures than either coarse or fine pearlite.

6. Any excessive amount of free ferrite at grain boundaries is especially susceptible to impact at low temperatures.

The following conclusions are submitted for consideration.

1. The orientation of the pearlite lamellæ in relation to the direction of the impact stress will be found to have a considerable effect upon resultant values.

2. Different components (cementite, ferrite, etc.,) having different coefficients of contraction due to lowering of temperature, may cause minute strains in the structure which reach a maximum near a temperature of —28 to —29 degrees Cent. (—18 to —20 degrees Fahr.).

3. These coefficients may be constant down to —18 to —20 degrees Fahr., but not below that temperature.

There is a vital need for more information concerning the behavior of metals at low temperatures.

For the sake of economy the factors of safety in design must be lowered, and with airplane, automobile and railroad transportation demanding the utmost resistance in the severe winter in many parts of

the continent, there is an important field of investigation in the low temperature, as well as the high temperature field.

Acknowledgments

The success of these tests is largely due to the kind permission and able assistance accorded by A. H. Eager, the general superintendent of motive power and car equipment, of the Canadian National Railways at Winnipeg, Manitoba. The authors also wish to acknowledge their appreciation and thanks to J. N. Finlayson, professor of civil engineering, and director of the engineering testing laboratories, University of Manitoba, for his interest and for the use of the facilities of the laboratory. We are also indebted to E. N. Johnson, track maintenance engineer, Canadian National Railways, Winnipeg, for encouragement and information and to R. Smith, works manager, Manitoba Rolling Mills, Selkirk, Man., for rolling some of the billets used, and to the American Rolling Mills for the supply of open-hearth iron used in the tests.

DISCUSSION

Written Discussion: By Alan E. Cameron, professor of metallurgy, University of Alberta, Edmonton, Alberta, Canada.

The authors' paper forms a timely and welcome addition to the very limited literature on this important subject. The effect of elevated temperatures upon the properties of metals has received considerable attention in the past and will doubtless continue to do so in the future. But the equally if not more important subject of low temperature effects has been woefully neglected. Failure of steel rails, or axles or other rolling stock parts due to low temperature brittleness probably has been the direct cause of more accidents than we realize. It is to be hoped that this very interesting paper will give further impetus to detailed study of this subject.

The authors' investigations have brought to light a very interesting fact in the apparent reversal of impact-resistance at temperatures in the neighborhood of —20 degrees Fahr. That the reversal is only temporary, however, should, perhaps, be emphasized more than is done in the paper. The persistence of this minimum point throughout practically all the steels tested is an interesting feature.

Further interest is added when it is shown that this minimum persists even after heat treatment. I reproduce herewith two tables of results presented by Morrison and myself in the paper referred to by the present authors. Note that in the majority of cases the lowest recorded Charpy value is at —18 degrees Fahr. and in all but one case it is at either —10 degrees Fahr. or —18 degrees Fahr. The significance of this fact was not apparent to us at the time, we assuming it was probably largely experimental error, but the presence

of a critical temperature appears definitely substantiated by the present authors' results. The establishment of this critical temperature for minimum impact-resistance throws considerable light on what has heretofore been a debatable point in this district (Edmonton, Alberta), namely, that street car axle and rail failures do not tend to occur at the periods of low atmospheric temperatures such as —35 or —45 degrees Fahr. but are much more frequent during spells

Table III

Heat Treatment—Experimental Results
Charpy impact tests on steel "A" (Carbon 0.10 per cent)

Quenched at 1650° F.		Quenched at 1650° F. Drawn at 440° F.		Quenched at 1650° F. Drawn at 810° F.		Quenched at 1650° F. Drawn at 1175° F.		Normalized at 1650° F.	
Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.
+68	49.5	+68	54.0	+68	61.5	+68	67.0	+68	67.0
+12	52.5	+12	57.5	+12	59.5	+12	69.5	+12	51.5
— 3	43.0	— 3	52.0	— 2	55.0	— 2	61.5	— 2	50.5
—10	43.5	—10	50.5	—10	50.5	—10	60.5	—10	19.0
—18	44.5	—18	58.5	—18	58.5	—18	62.5	—18	6.0
—22	49.5	—22	58.5	—23	58.5	—23	64.0	—22	6.0

of intermediate temperature, namely those around —10 to —20 degrees Fahr.

I have little comment to make on the conclusions offered by the authors. They seem well founded on the results of the investigations. Their suggestion that the different components may have different coefficients of contraction and cause intercrystalline strain is interesting. It would help to explain the great decrease in impact-resistance with increasing carbon content. Grain size is un-

Table IV

Heat Treatment—Experimental Results
Charpy impact tests on steel "B" (Carbon 0.34 per cent)

Quenched at 1575° F.		Quenched at 1575° F. Drawn at 440° F.		Quenched at 1575° F. Drawn at 810° F.		Quenched at 1575° F. Drawn at 1175° F.		Normalized at 1575° F.	
Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.	Temp. of Test, °F.	Charpy Value, Ft. Lb. per Std. Spec.
+68	26.5	+68	16.5	+68	30.0	+68	42.0	+68	29.0
+12	11.0	+12	14.0	+12	25.5	+12	31.5	+12	20.7
— 4	10.5	— 4	12.5	— 4	24.0	— 4	26.5	— 3	18.0
—10	8.0	—10	14.0	—10	22.0	—10	27.0	—10	17.5
—18	12.0	—18	9.5	—18	21.5	—18	26.0	—18	8.0
—25	15.0	—25	9.5	—26	21.0	—26	31.0	—24	9.0

doubtedly of prime importance in impact-resistance. Morrison and I also noted that a granular or crystalline fracture indicating intercrystalline failure was characteristic of Charpy breaks under low temperature conditions. I should like to point out that the present authors' results on low carbon steel (rivet steel) do not agree with our results on normalized 0.10 per cent carbon steel. This is clearly shown in our Table III reproduced herewith.

CHAIRMAN R. S. ARCHER:[1] It seems there are several interesting points

[1]A. O. Smith Research Corp., Milwaukee.

here, one of which is the new, or at least little known, reversal in impact properties around minus 25 to 30 degrees Fahr.

The fact that these papers have been presented to us today indicates the interest in low temperature properties of metals. No one has said anything about aircraft. This subject is of great importance in aircraft construction and use. We have several fields to consider—the railroads, the low temperature refrigeration equipment, aircraft, and in some cases even our own automobiles.

In referring to the discrepancy pointed out in the discussion by Cameron on the 0.10 per cent carbon steel, I would like to ask Mr. Gilchrist what condition the 0.10 per cent carbon rivet steel was in.

MR. GILCHRIST: The rivet steel was "as rolled."

CHAIRMAN ARCHER: It would seem that that might have considerable bearing on the matter. Table III quoted by Cameron shows excellent markings of impact properties in quenched and drawn materials, but a marked falling-off again at minus 10 degrees in the case of normalized material. It seems quite likely that the hot-rolled material referred to by Mr. Gilchrist may have differed in two ways from normalized material. It may have had some heat treatment effect and it may also have had some fiber or elongation of grain structure, which might assist very much in maintaining toughness at the low temperature.

With reference to the impact test, I believe we are aware that in many steels we are dealing really with a notch test and not with an impact test.

In the case of the temper brittleness of nickel-chromium steels, it was pointed out that slow bend tests on notched specimens gave substantially the same results as the impact tests on notched specimens, and that this slow bend test would reveal the temper brittle condition just as well. On the other hand I believe there are certain steels, or certain lots of steel, and that includes some low carbon material, possibly somewhat high in phosphorus, in which the rate of loading is also quite important, so we are really dealing with a specific test which certainly includes the effect of notches and may or may not include the effect of loading.

On behalf of the meeting I wish to thank the authors for this paper. Our friends in Canada are in a better position than most of us to study and to appreciate the low temperature phenomena. It is very good that they bring it to our attention.

T. S. FULLER:[2] Mr. Cunningham and Mr. Gilchrist have expressed their impact results in terms of foot-pounds per square inch. Our consideration of the impact test has led us to believe that there is very little significance to that term. When one considers the anomalies of this test which have been pointed out by Max Moser in an article published in the TRANSACTIONS of this Society in 1925, Vol. 7, pp. 297-320, in which he reported tests on impact specimens of the same material in different cross sections, where a material having the standard cross section may give a value of 50 foot-pounds absorbed, and the same material having double the cross section may still give a value of 50 foot-pounds absorbed, the term "foot-pounds per square inch" loses its significance.

[2]Research laboratories, General Electric Co., Schenectady, N. Y.

Authors' Closure

We are pleased that Prof. Cameron has offered such a welcome discussion and glad to know that his experience with low temperature effects upon steel and iron tends to bear out our findings. It is true the reversal to impact at about —20 degrees Fahr. is only temporary, but this point seems to be critical and further lowering of temperature brings uncertain results for a certain range. The results on 0.10 per cent carbon rivet steel are not the same as those of his, owing we believe to the velocity of the blow 10.2 feet per second for Izod as against 17.39 feet per second for the Charpy. The higher velocity[3] would likely fracture completely the tough specimens whereas our fractures were not complete until —29 degrees Fahr. were reached. Also a rough check on the 0.10 per cent carbon rivet steel after normalizing at 1650 degrees Fahr. cuts our original impact values approximately in half. We did not complete enough specimens to give any definite conclusions. Further experiments are being carried out to find if possible whether the different components do vary in the coefficient of contraction.

Mr. Fuller questions the use of the term "foot-pounds per square inch." True, there is very little significance to the term from the designer's point of view. The unit values for notched bar specimens in impact is somewhere between the square and the cube of the area. The authors do not consider that this detracts from the results as the velocity at impact,[4] carefully milled notches, uniform specimen size and each placed in the machine vise by means of a jig gage, means that our relative values are dependable, for after all, in its present state the impact test is purely a relative one and only indirectly of use to designers.

Mr. Archer mentions the omission of aircraft. The authors think that aircraft requirements are really behind the present impetus being given to the investigation of the low temperature properties of metals. Any one who has witnessed the start off of a mail plane in a ground atmosphere of —35 to —40 degrees Fahr., if metallurgically inclined, wonders just what the metals have really to stand. Shock and vibration we believe are the most important stresses to which aircraft are subjected.

The closing remarks by Mr. Archer throw further light upon the reason for the different results the 0.10 per cent carbon rivet steel show when compared to those of Morrison and Cameron. There is no doubt that a straight normalizing of most steels is accompanied by a marked falling off in shock resistance. The material used in the "as-rolled" condition gave a fracture of fibrous appearance whereas a normalized bar of the same material does not show that condition so markedly.

Low temperature properties of metals are very vital to the great central portions of Canada and we have shown something of our problem, to our friends in the south. They supply a great deal of the metal which we have to use, and if "cold brittleness" is a characteristic of the metals, then the demand might come to change these characteristics if possible.

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[3]Hadfield and Main, "Shock Tests and Their Standardization," Institute of Civil Engineers Proceedings, 1920.

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[4]"Applied Elasticity," Timoshenko and Lessells 1st ed. Westinghouse Technical Night School Press, East Pittsburgh, Pa., 1925.

AGE HARDENING PHENOMENA IN TYPICAL FUSION-WELD METAL

By F. R. Hensel and E. I. Larsen

Abstract

This paper deals with age hardening phenomena in arc welds caused by the precipitation of iron-nitrogen compounds. The changes in hardness, magnetic properties, electrical conductivity, and tensile properties as well as the structural changes have been investigated. The properties of arc welds are compared with those of gas welds, low carbon steel and ingot iron.

Introduction

THE usual metallic arc weld deposits are, according to their chemical analysis, nearly pure iron. Their behavior, however, differs greatly from that of pure iron in that their physical properties can be changed considerably by suitable heat treatments. They have a tendency to embrittlement due to the fact that they possess age hardening properties which is an indication that they are not pure metals, but metastable solid solution alloys. In the arc welding process, oxygen and nitrogen, the two main constituents of the air, are ionized and enter the deposited metal either in the form of oxides and nitrides or through absorption by the molten steel.

In recent years the problem of the influence of gases upon the physical properties of metals has been studied by a number of investigators and it is hoped that the results of this paper are another step in the direction of solving this problem definitely. It must be pointed out that this investigation is not yet complete and that this paper, therefore, may be regarded only as a progress report.

Materials

Most of the tests were made on pads obtained by a deposition of commercial bare welding wire. A few tests were made on commercially available "V" arc welds prepared by special processes and

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by the use of special coatings. Comparisons were made between these and gas welds and atomic hydrogen welds. Ingot iron and some low carbon steels were included in this investigation as seen from Table I. The chemical analysis of most of the materials used for tests are recorded in Table II.

Table I
Test Materials

Mark	Description	Ampere
"A"	Metallic arc welded pad, uncoated wire (0.02%C),	175
"C"	Metallic arc welded pad, uncoated wire (0.29%C),	175
H 46	Metallic arc welded pad, uncoated wire (0.02%C),	150
H 47	Metallic arc welded pad, uncoated wire (0.02%C),	250
H 48	Metallic arc welded pad, coated wire .....,	200
H 54	Metallic arc welded pad, coated wire .....,	800
H 92	Metallic arc welded pad, uncoated wire (0.02%C),	200
V 134	Metallic arc welded pad, uncoated wire (0.02%C),	...
"E"	Low carbon steel plate, V-weld,	250
"F"	Low carbon steel plate, V-weld,	225
"G"	Low carbon steel plate, V-weld,	...
H 65	Carbon arc weld pad,	500
H 66	Carbon arc weld pad,	600
H 38	Oxyacetylene welded pad	
H 39	Atomic hydrogen welded pad	
H 56	Ingot Iron	
H 57	Izett-Steel (Special Krupp material)[2]	
H 58	Handpuddled wrought iron.	

[2]A. Fry: Kruppsche Monatshefte 7 (1926), pp. 185-196
U. S. P. 1,729,378
U. S. P. 1,700,674
M. Ulrich: Z. Bayer, Rev.-V. 32 (1928), No. 5, pp. 53-57, 68-72
O. Bauer and H. Arndt, Z. Bayer, Rev.-V. 32 (1928) No. 21
pp. 292-295 pp. 306-308

Table II
Chemical Analysis of Test Materials

Mark	C	Si	Mn	S	P	Al	W	Slag
Arc weld H92	0.02	0.037	0.02	0.037	0.010	....	....	....
Arc weld "A"	0.027	0.004	0.006	0.03	0.016	0.006	....	....
Arc weld "C"	0.028	0.003	0.27	0.035	0.010	0.003	....	....
Oxyacetylene weld H38	0.033	0.003	0.14	0.021	0.027	0.006	....	....
Atomic Hydrogen weld H39	0.033	0.008	0.15	0.008	0.005	0.009	0.26	....
Ingot Iron H56	0.02	0.008	0.04	0.043	0.009	....	....	....
Izett Steel H57	0.15	0.06	0.54	0.039	0.025	0.06	....	....
Wrought Iron H58	0.015	0.044	0.035	0.009	0.016	....	....	2.96

With the exception of Izett steel the C, Si, S and P contents of the various materials are of approximately the same magnitude.

Gas analyses were made by N. A. Ziegler[1] by means of the vacuum fusion method. Nessler's reagent was used for the determination of nitrogen by E. W. Beiter.[1] The essential parts of the

[1]Research Engineer, Westinghouse Research Laboratories.

latter method are: solution in hydrochloric acid, nitrogen compounds being reduced to ammonia and combined with the acid to form ammonium chloride. The ammonia is displaced by caustic and distilled from the resulting ferrous hydroxide.

Color is developed by Nessler's reagent and compared with that produced by a standard ammonia solution. The nitrogen is calculated from the ammonia content. It is obvious that by the latter method only the nitrogen in form of iron or manganese nitrides[2] is determined while the vacuum fusion method gives the combined nitrogen and the nitrogen that is dissolved, adsorbed or mechanically held in pores or blow holes. The fairly close agreement of the results as found by both methods is seen from Table III. The data obtained by means of Nessler's reagents are somewhat on the high side.

Table III
Gas Analysis of Test Materials

Mark	O_2 Vacuum Fusion Gas Analysis*	N_2 Vacuum Fusion Gas Analysis*	H_2	N_2 Nessler's Reagent
Arc weld H92	....	....	....	0.143
Arc weld "A"	0.259	0.127	....	0.147
Arc weld "C"	0.183	0.093	....	0.128
Arc weld H46	....	....	....	0.162
Arc weld H47	....	....	....	0.145
Arc weld H48	....	....	....	0.129
Arc weld V134	0.785 (slag!)	0.171	0.003	0.139
Oxyacetylene weld H38.	0.054	0.013	....	0.024
Atomic Hydrogen weld H39	0.053	0.017	0.005 (high!)	0.037
Ingot Iron H56	0.08	0.004	....	0.0065
Izett Steel H57	0.00	0.00	....	0.0064 0.0045 0.0053

*Proceedings, Institute of Metals Division, A.I.M.E., 1928, p. 544.

Age Hardening Experiments

The influence of nitrogen upon the properties of welds is still much discussed, although recent investigations have thrown more light upon it. That the iron-nitrogen system is an age hardening system is evident from the tentative diagram by Fry[3] and Epstein[4], shown in Fig. 1. This diagram is not an "equilibrium" diagram, as the iron-nitrogen alloys are unstable and equilibrium conditions

[2]Jordan, Swindells, Bureau of Standards Scientific Paper No. 457 (1922).

[3]Kruppsche Monatshefte, 1923, p. 138.

[4]Samuel Epstein, "Observations on the Iron-Nitrogen System," Transactions, American Society for Steel Treating, Vol. XVI, No. 5, 1929, p. 19-65.

cannot be determined without taking account of the partial pressure of active nitrogen in the system.

The line x in Fig. 1 indicates the approximate nitrogen content of metallic arc welds made with a bare wire. According to the diagram, arc welds would have to be heated to about 600 degrees Cent. (1110 degrees Fahr.) to be well within the alpha-solubility range

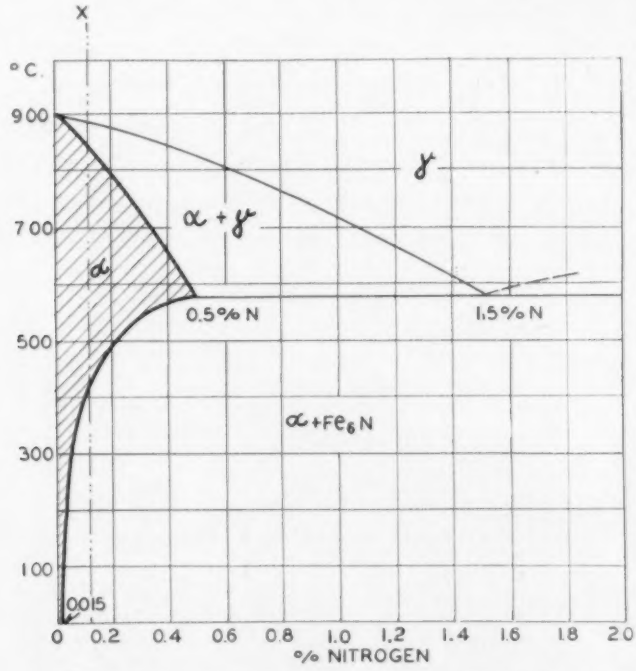


Fig. 1—Iron-Nitrogen Diagram According to Fry and Epstein.

before quenching in order to develop fully their age hardening properties. As a result of aging the constituent Fe_6N will be precipitated in submicroscopic dispersion and cause embrittlement of the metal by blocking the slip planes and thereby obstructing plastic yielding.

The tempering-hardness relations of arc welds are shown in Fig. 2. The test samples were quenched from different temperatures and the resulting hardness was measured. The increase in hardness with the quenching temperature becomes very pronounced at 500-600 degrees Cent. (930-1110 degrees Fahr.). Above that temperature the hardness decreases.

The effect of various aging temperatures following quenching from 600 degrees Cent. (1110 degrees Fahr.) is seen from Fig. 3. The maximum hardening effect occurs at room temperature. Aging

in ice gave the same results as aging at 25 degrees Cent. The greatest hardness is reached after approximately 50-60 hours and no appreciable change of hardness occurs with further aging. Higher aging temperatures, e.g., 100, 200 and 300 degrees Cent. (210, 390, 570 degrees Fahr.) produce no increase in hardness above that

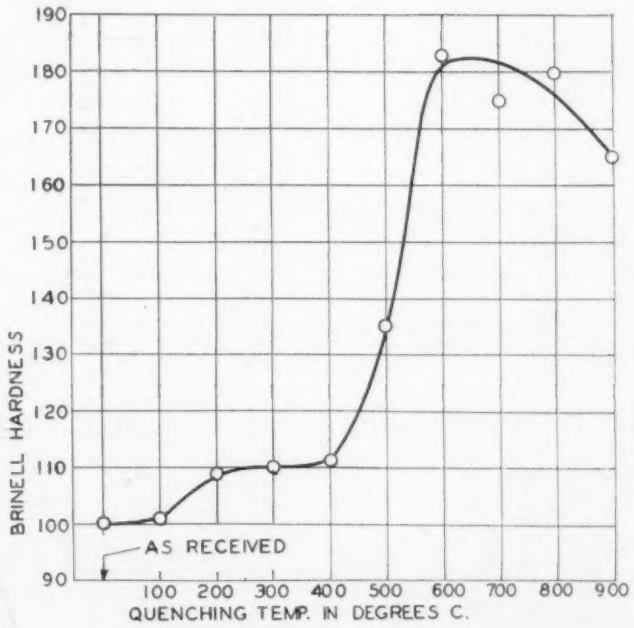


Fig. 2—Effect of Various Quenching Temperatures on the Hardness of an Average Arc Weld.

reached by quenching and the hardness decreases slowly at 100 degrees Cent. aging temperature, more rapidly at 200 degrees Cent. and extremely rapidly at 300 degrees Cent.

The effect of different quenching temperatures on the hardness reached during aging at room temperature is given in Fig. 4. A quench from 600 degrees Cent. (1110 degrees Fahr.) produces the maximum hardness. The trend is downward with increasing quenching temperatures.

Fig. 5 shows aging hardness curves of five commercial welds made with bare wire. All exhibit the same general aging characteristics. Aging of arc welds can be greatly reduced if protective coatings and special techniques are employed. This is evident from Fig. 6. The susceptibility to embrittlement is apparently a function of the nitrogen content of the metal. In Fig. 6, therefore, the right hand ordinate shows the amount of nitrogen necessary to produce the hardness values indicated on the left hand ordinate of the dia-

gram. Some of the data in Fig. 6 are taken from a paper by Eilender and Wasmuth.[5] In general our data check their results. Small discrepancies are due to the fact that they used pure iron, while for this investigation arc welds were employed which are not

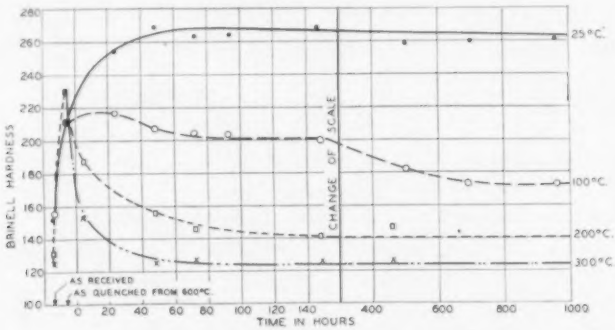


Fig. 3—Effect of Various Aging Temperatures on the Hardness of Metallic Arc Weld "A" After Quenching from 600 Degrees Cent. (1110 Degrees Fahr.).

homogeneous and which contain a high percentage of oxygen. The increase in nitrogen above a certain percentage apparently does not increase the hardness in the same proportion and arc welds con-

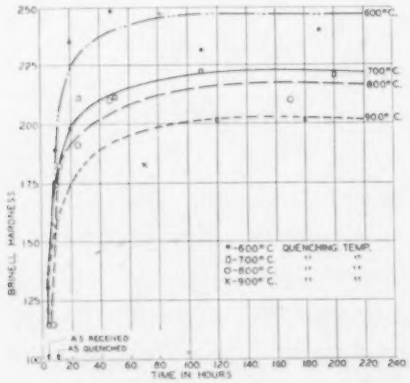


Fig. 4—Hardness of Weld Samples "A" After Quenching from Different Temperatures and Aging at Room Temperature.

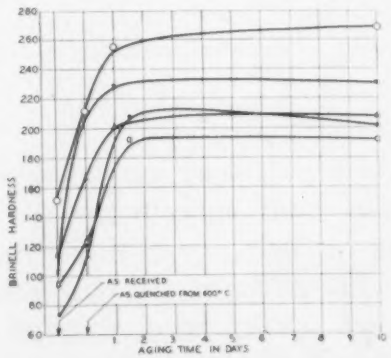


Fig. 5—Time-Hardness Curves of Arc Welds Quenched from 600 Degrees Cent. (1110 Degrees Fahr.) and Aged at Room Temperature.

taining between 0.06 and 0.14 per cent nitrogen do not show appreciable differences in their age hardening properties. If, therefore, "improvements" of welds are to be accomplished the nitrogen content must not exceed the lower limit of 0.06 per cent N. Improvements mean a decrease of the nitrogen or gas content.

The most practicable means of accomplishing that is, according

[5]Arch. Eisenhüttenw., Vol. 3, 1930, p. 662.

to our present knowledge, coatings and fluxes which fulfill two chief conditions:

(1) Creation of a protective reducing atmosphere containing large amounts of free hydrogen.

(2) Formation of a suitable slag having low melting point, low viscosity and low density.

Gas welds and atomic hydrogen welds are apparently low enough in nitrogen to make their aging characteristics of minor importance for practical purposes.

The difference between weld-metal deposited in a V-groove

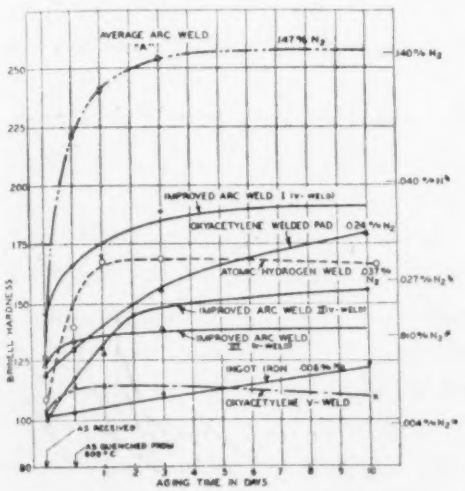


Fig. 6—Effect of Nitrogen Content on Age Hardening Properties of Different Welds.

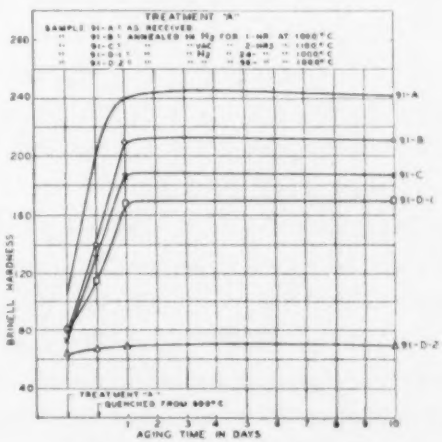


Fig. 7—Effect of Degasifying Treatments on Aging of Metallic Arc Welds.

and in form of pads was quite noticeable. As might be expected, much better properties were obtained with weld-metal taken from a V-groove.

For a comparison the slight amount of aging of ingot iron is shown in the same diagram, Fig. 6.

The effect of degasifying treatments in hydrogen and vacuum upon the age hardening properties of an arc deposited metal are shown in Fig. 7. After a hydrogen treatment at 1000 degrees Cent. (1830 degrees Fahr.) for four days the weld has lost its age hardening properties nearly completely. The proof that this treatment causes a loss in nitrogen is given in Table IV.

This fact was reported previously by Walsted[6] who found that

[6] *Journal*, American Welding Society, Vol. 8, Nov., 1929, p. 31-32.

Table IV
Effect of Degasifying Treatments

Mark	Treatment	Nitrogen Content Before Treatment Per Cent	Nitrogen Content After Treatment Per Cent
H92—tensile test piece; 0.505 inch diameter	4 days at 600 degrees Cent. in hydrogen.	0.142	0.106
H92—tensile test piece; 0.505 inch diameter	4 days at 1000 degrees Cent. in hydrogen.	0.142	0.030
H92—chips	1 day at 1000 degrees Cent. in hydrogen.	0.142	0.020

hydrogen combining with nitrogen in steel forms ammonia. Further, Epstein[7] and McQuaid[8] pointed out the instability of iron nitrides which results in a gas evolution at temperatures as low as 300 degrees Cent.

Although it seems to be beyond doubt that nitrogen is the cause of age hardening, it might be well to discuss very briefly the influence of oxygen[9] and carbon with respect to age hardening.

The type and degree of age hardening caused by carbon is represented by the ingot iron sample in Fig. 6. The investigated welds all contain about the same amount of carbon as ingot iron, a fact which rules carbon out immediately.

Oxygen seems to cause a certain amount of aging as shown by Eilender and Wasmuth[5], the amount, however, being very small and decreasing to practically nothing with oxygen contents above 0.70 per cent. Although their results are not very consistent they prove that the effect of oxygen on the aging phenomena of arc welds is negligible and there is only nitrogen left as a probable cause.

Change of Physical Properties During Aging

a. *Tensile Properties.* In dealing with tensile properties of arc welded pads we are confronted with the difficulty of obtaining comparable results on account of the nonhomogeneity of the material. All of the pads used in this investigation were carefully prepared and,

[7]Samuel Epstein, "Observations on the Iron-Nitrogen System," Transactions, American Society for Steel Treating, Vol. XVI, No. 5, 1929, p. 21.

[8]H. M. McQuaid, "Discussion of Observations on the Iron-Nitrogen System," by Samuel Epstein, Transactions, American Society for Steel Treating, Vol. XVI, No. 5, 1929, p. 63.

[9]Gerald Brophy, *Journal*, American Welding Society, Vol. 6, No. 9, 1927, p. 67. Alexander, *Journal*, American Welding Society, Vol. 8, No. 9, 1929, p. 94.

as can be seen from the following tables, fairly good results were obtained. The tensile properties of series V-134 were rather poor. The tensile data of these pads are not given, although it may be mentioned that it was possible to correlate these data by plotting them as a function of the specific gravity, in which case the specific gravity is a measure of the soundness of the material. From Fig. 8 it is evident that there is a steady increase of the tensile strength with specific gravity which points strongly to the importance of the soundness of the material. Furthermore, the interesting fact was revealed that the tensile strength at elevated temperatures is from 5000 to 10,000 pounds per square inch higher than at normal temperatures for test pieces having the same specific gravity. This is probably a measure of the blue heat brittleness of the arc welded pads V-134.

Tables V to VII and Figs. 8 to 12 give the tensile test data on metallic arc welds, atomic hydrogen welds, oxyacetylene welds and some low carbon steels (ingot iron, Izett steel, wrought iron) after the following treatments: (1) As received, (2) As quenched from 600 degrees Cent. (1110 degrees Fahr.), (3) As quenched from 600 degrees Cent. and aged at room temperature.

Standard tensile specimens having 2-inch gage length and 0.505 inch diameter were used for all tensile tests except those on oxyacetylene and atomic hydrogen welds. In the latter case a sample having 0.250 inch diameter and 1-inch gage length was used because of the small amount of material available.

Samples of pad "A" show an increase in ultimate strength after quenching which decreases rapidly with aging, while pad "C" shows

Table V
Tensile Properties of Arc Welded Pads "A" and "C"

Mark	Treatment	Yield Point Pounds per Square Inch	Ultimate Strength Pounds per Square Inch	Elongation in 2 Inches Per Cent	Reduction Area Per Cent
	As-received	38,500	55,000	13.5	15.0
"A"	Quench 600 degrees Cent.	39,700	57,250	11.0	15.4
		40,000	80,000	0	0
Bare wire 175 Amperes		10,800	70,500	0	0
	Aged 8 days	.....	30,000	0	0
		.....	58,500	0	0
		43,750	56,250	9.0	15.9
"C"	As-received	46,500	61,700	10.0	25
		32,500	89,000	2.5	5.0
Bare wire 175 Amperes	Quench 600 degrees Cent.	46,000	92,250	3.6	5.0
		24,500	103,250	1.5	2.3
	Aged 8 days	29,500	95,000	1.0	1.2

an increase in ultimate strength not only after quenching, but after subsequent aging as well. In one case the relatively high value of 103,250 pounds per square inch ultimate strength was reached. The elongation values of the quenched and aged specimens decrease to

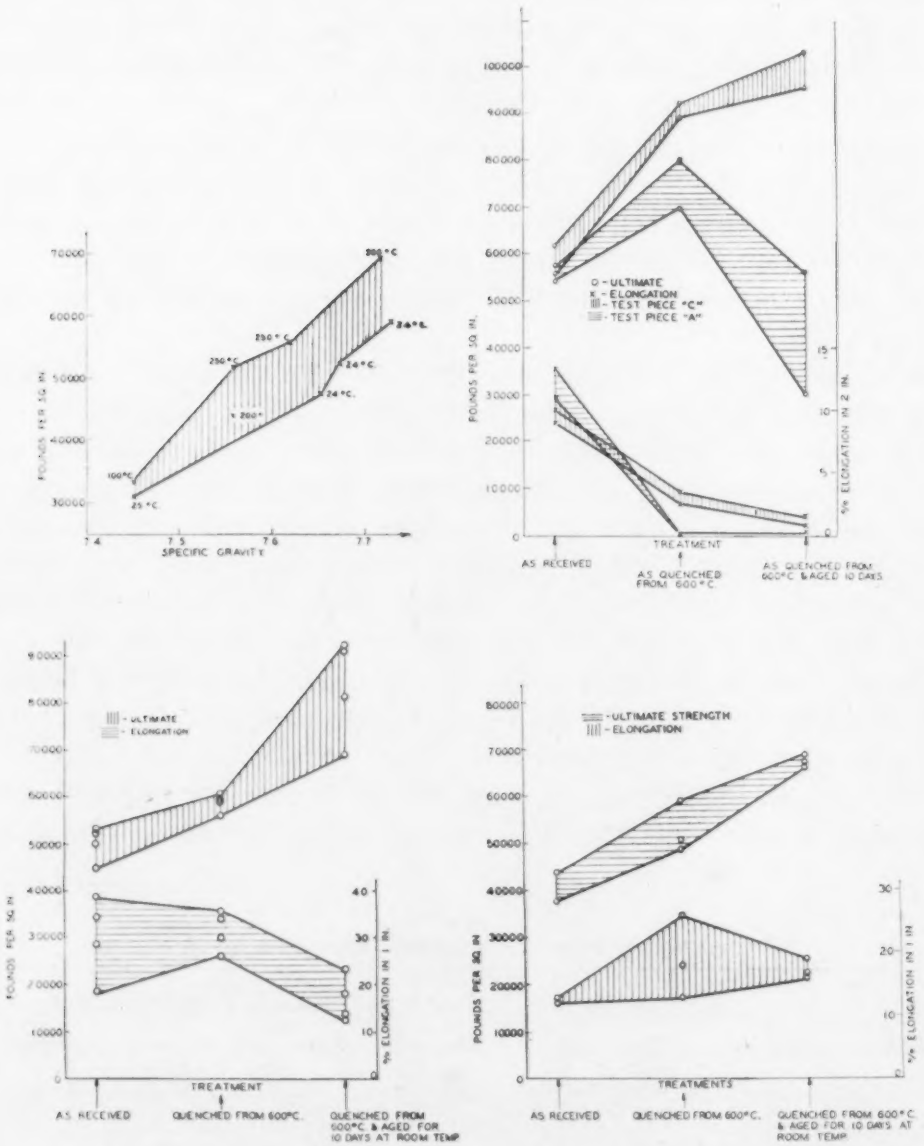


Fig. 8—Relation of Ultimate Strength to Specific Gravity of Arc Weld V-134 Tested at Various Temperatures.

Fig. 9—Effect of Heat Treatment on Ultimate Strength and Elongation of Test Pieces Cut from Metallic Arc Weld Pad.

Fig. 10—Effect of Heat Treatment on Ultimate Strength and Elongation of Test Pieces Cut from Oxyacetylene Weld Pad H-38.

Fig. 11—Effect of Heat Treatment on Ultimate Strength and Elongation of Test Pieces Cut from Atomic Hydrogen Weld Pad H-39.

practically zero. The conditions can be clearly seen from Fig. 9.

The stress-strain characteristics were automatically drawn by an Amsler testing machine. The samples in the "as-received" condition showed a definite yield point while none was detected after the heat treatment, the stress-strain curves being characteristic of a brittle material which fails with practically no yielding.

In Table VI the tensile properties of arc welds H46, H47, H48 and H54 are given. The same embrittlement characteristics are evident.

Table VI

Tensile Properties of Arc Welds H46, H47, H48, H54

Mark	Heat Treatment	Ultimate Strength Pounds Per Square Inch	Elongation Per Cent	Reduction of Area Per Cent	Brinell
"H46"	As-received	56,500	2.5	4.7	...
Bare wire		53,500	2.3	4.0	...
150 Amperes	Quench 600 degrees Cent.	83,750	0	0	...
		85,700	0	0	...
	Aged 10 days	51,300	0	0	...
		66,400	0	0	...
		51,750	5.6	4.9	126
"H47"	As-received	52,900	7.9	7.2	116
	Quench 600 degrees Cent. and aged one day	64,400	0.8	0	235
Bare wire		45,900	?	0	255
250 Amperes	Aged 10 days	24,000	0.2	0	255
		55,400	15.0	22.2	111
"H48"	As-received	51,150	10.0	15.1	111
	Quench 600 degrees Cent. and aged one day	85,000	0.9	0	212
Coated wire		86,000	0.9	0	218
200 Amperes		86,000	1.7	0	...
	Aged 10 days	91,800	0.3	0	269
		60,000	3.6	6.5	149
"H54"	As-received	46,000	1.7	3.8	123
	Quench 600 degrees Cent. and aged one day	73,150	0.5	0	230
Coated wire		65,800	0.5	0	225
800 Amperes		71,700	0.6	0	230
	Aged 10 days	80,750	1.0	0	235

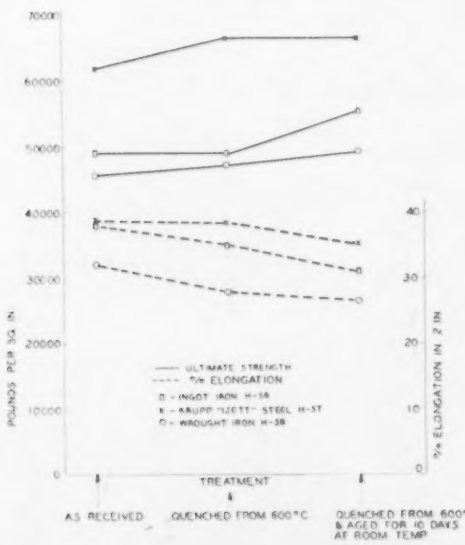
The cases in which we obtain low ultimate strength, although the Brinell hardness is high, may be attributed to faulty material. Coating of the rods in samples H48 and H54 did not prevent embrittlement, probably because of improper selection of coating material.

The values given in Table VII are mean values of 3 to 4 tests for each treatment. All test data were used for plotting the curves shown in Figs. 10 and 11. The changes of the atomic hydrogen weld specimens are relatively small and indicate the absence of embrittlement. The oxyacetylene pad, H38, showed a pronounced increase in ultimate strength. The elongation values decreased by

Table VII

Tensile Properties of Pads H38, H39

Mark	Heat Treatment	Ultimate Strength Pounds Per Square Inch	Elongation 1 Inch Per Cent	Reduction of Area Per Cent
"H38" Oxyacetylene weld	As-received	49,750	30.5	60.2
	Quench 600 degrees Cent.	56,600	32.0	67.5
		83,600	17.5	40.5
	Aged 8 days	40,500	12.5	22.5
"H39" Atomic hydrogen weld	As-received	52,600	19.0	34.3
	Quench 600 degrees Cent.	67,100	17.0	50.6
	Aged 8 days			


POUNDS PER SQ. IN.
% ELONGATION IN 2 IN.
ULTIMATE STRENGTH
% ELONGATION
O - INGOT IRON H-38
X - KRUPP "IZETT" STEEL H-37
O - WROUGHT IRON H-38
TREATMENT
AS RECEIVED
QUENCHED FROM 600°C.
QUENCHED FROM 600°C. & AGED FOR 10 DAYS AT ROOM TEMP.

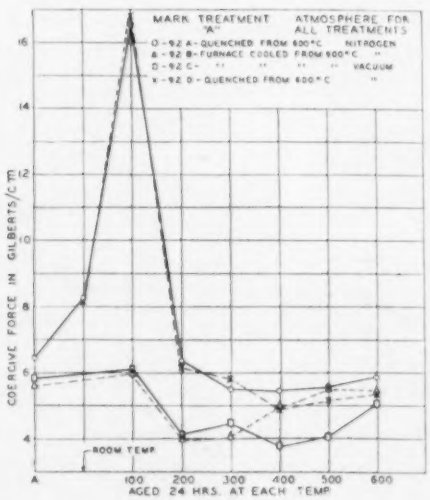

MARK TREATMENT "A"
ATMOSPHERE FOR ALL TREATMENTS
O - 92 A - QUENCHED FROM 600°C NITROGEN
Δ - 92 B - FURNACE COOLED FROM 600°C "
□ - 92 C - " " " " VACUUM
X - 92 D - QUENCHED FROM 600°C "
COERCIVE FORCE IN GILBERTS/CM
ROOM TEMP.
AGED 24 HRS. AT EACH TEMP.

Fig. 12—Effect of Heat Treatment on Ultimate Strength and Elongation of Ingot Iron, Krupp "Izett" Steel and Wrought Iron.

Fig. 13—Change of Coercive Force During Aging at Various Temperatures on Quenched and Slowly Cooled Metallic Arc Welds.

approximately 40 per cent of their original values but are still in the neighborhood of 20 per cent.

The atomic hydrogen sample is not embrittled by aging, according to the tensile data, although the gas analysis indicates that it contains more nitrogen than the oxyacetylene weld.

Nitrogen content alone is not an infallible indicator of susceptibility to aging. The primary requirement for age hardening is a decrease of the solid solubility with temperature of some component of the alloy in question. If, by some means, the solid solubility of iron for nitrogen is increased—as might be possible by adding alloy-

ing elements—a decrease in aging effects will consequently be the result.[10]

For a comparison the changes of the physical properties of ingot iron, Izett steel and wrought iron are plotted in Fig. 12.

All three materials age somewhat. The amount of embrittlement, however, is so slight in all of them that it is hardly comparable with that encountered in arc welds.

Tensile tests were also made on carbon arc welded pads but the unsoundness of the material caused the results to be quite erratic. The material, however, exhibited marked aging characteristics, the Brinell hardness increasing from 90 to 210 and the elongation dropping to zero, as a result of aging effects.

b. *Impact Values.* A series of impact tests was run to check the tensile test results. The data are given in Table VIII. Each value is the mean of 4 to 6 tests made after each heat treatment. The

Table VIII
Impact Values of Various Welds

Mark	Heat Treatment	Average Foot-Pounds to break in single blow
"H38"	As-received	33.8
Oxyacetylene	Quench 600 degrees Cent.	38.0
	Aged 8 days	8.3
"H39"	As-received	68.0
Atomic Hydrogen	Quench 600 degrees Cent.	70.3
	Aged 8 days	79.0
"H46"	As-received	2.5
Metallic Arc	Quench 600 degrees Cent.	2.0
(Uncoated wire)	Aged 10 days	1.7
"H66"	As-received	10.0
(Carbon Arc	Quench 600 degrees Cent.	2.7
very unsound)	Aged 10 days	1.0
"G"	As-received	4.4
V-weld	Quench 600 degrees Cent.	5.3
	Aged 2 days	2.6

results obtained were similar to those revealed by the tensile tests. In a number of cases the impact values increase after quenching, but drop considerably after aging. The velocity of precipitation seems to be slightly different in the various materials. The atomic hydrogen weld exhibited rather high impact values and showed no detrimental aging effects. The impact strength increased after a treatment that embrittles the ordinary arc weld.

[10] W. E. Ruder and G. R. Brophy, *Chemical and Metallurgical Engineering*, Nov. 9, 1921. H. H. Lester, TRANSACTIONS, American Society for Steel Treating, Vol. XVI, No. 5, 1929, p. 16-17.

c. *Magnetic Properties.* W. Köster[11] found that the coercive force is a sensitive indicator for the beginning of solid solubility changes as found in age-hardening systems. The coercive force of a supersaturated solid solution is increased during precipitation and the maximum coercive force is obtained when the particle size of the precipitate is of microscopical order. This is in agreement with Yensen's[12] theory stating that any factor that tends to distort the regular spacing of the atoms in the crystal lattice will cause a decrease in permeability and an increase in hysteresis loss if we assume that precipitation is accompanied by distortion of the space lattice at certain stages of the aging process. H. Esser and W. Eilender[13] set forth the theory that any precipitation is accompanied by a cold deformation of the space lattice, the effect of cold deformation being a function of the aging temperature. The effectiveness of cold deformation in producing alterations of physical properties will decrease with higher aging temperatures because the plasticity of the matrix metal increases.

The magnetic properties were investigated after two treatments:

(a) Furnace cooling from 900 degrees Cent. (1650 degrees Fahr.)[14] and aging at the various temperatures for 24 hours.

(b) Water quenching from 600 degrees Cent. (1110 degrees Fahr.) and subsequent aging at various temperatures for 24 hours.

The measurements were made on ring samples of 1 inch outside diameter, ¾ inch inside diameter, 1 inch length and on bars ⅛ inch square, 10 inches long. The rings were machined from welded pads and consisted entirely of weld metal. The bars were forged and hot-rolled from welded pads. Forging of the pads was attended with some difficulties. The microstructure of the specimen showed the major part of the contained nitrogen was in the form of small needles, the pearlite-like areas being scarce.

The heat treatments were conducted in nitrogen, hydrogen and vacuum. It was realized that a certain amount of nitrogen would

[11]Z. anorg. Chem. 179, 1929, p. 297-308.

[12]*Metals and Alloys*, May, 1930.

[13]*Arch. F. Eisenhüttenw.* (4), Heft 3, 1930, p. 113.

[14]The approximate cooling rate was 100 degrees Cent. per hour.

be lost during the long time treatments, but the loss was not thought to be sufficient to influence the accuracy of the results. Even if welds with 0.15 per cent N_2 are reduced in nitrogen content to 0.06 per cent N_2, the type of curves obtained with these two different N_2 percentages will be comparable.

After completing each heat treatment the test specimens were cooled in various ways, as in the furnace, in air, or water-quenched. The effect of the heat treatments on arc weld H92 containing 0.14

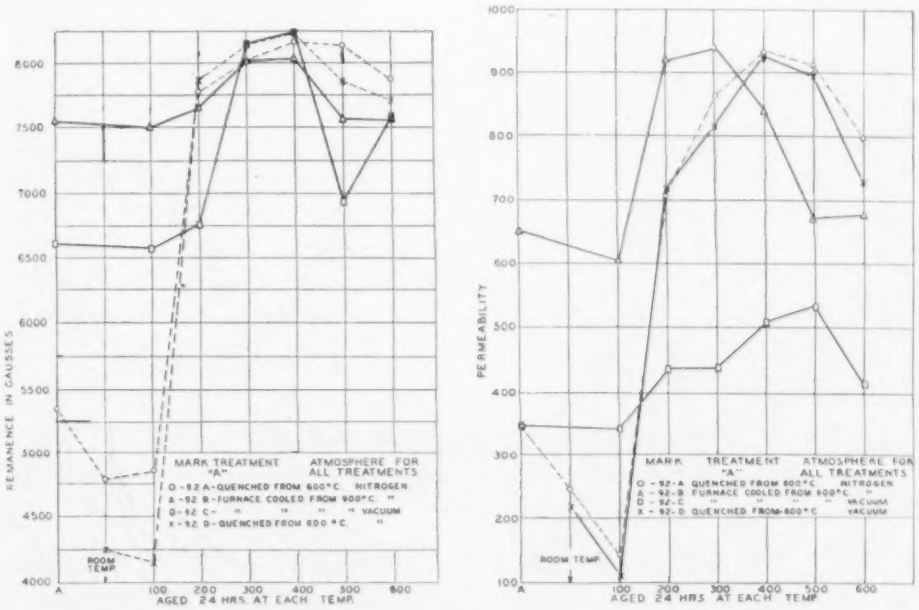
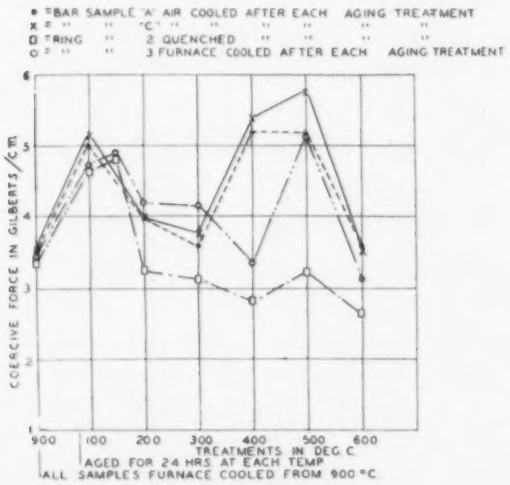


Fig. 14—Change of Remanence During Aging at Various Temperatures on Quenched and Slowly Cooled Metallic Arc Welds.
Fig. 15—Change of Permeability During Aging at Various Temperatures on Quenched and Slowly Cooled Metallic Arc Welds.

per cent N_2 are seen from the curves in Figs. 13, 14 and 15. In the "as-quenched" specimens the coercive force increases slightly with aging at room temperature. A pronounced increase occurs at 100 degrees Cent. aging temperature, which has completely disappeared after aging at 200 degrees Cent. Aging at higher temperatures decreases the coercive force still further, until a temperature of 300-400 degrees Cent. is reached. From this on the values show a slight tendency to rise again. In the "slowly cooled" specimens the increase in coercive force after aging at 100 degrees Cent. is small but there is a large decrease after aging at 200 degrees Cent. The coercive force increases again by aging at temperatures above 300-400 degrees Cent.

The permeability and remanence vary inversely with the coercive force. In both cases there is a surprisingly rapid increase in the permeability and remanence of the "as-quenched" samples after aging at 200 degrees Cent., the maximum being reached at 400 degrees Cent. aging temperature. In the samples "as slowly cooled from 900 degrees Cent." the values of remanence and per-


• = BAR SAMPLE "A" AIR COOLED AFTER EACH AGING TREATMENT
X = " " "C" " " " " " "
□ = RING " 2 QUENCHED " " " "
○ = " " 3 FURNACE COOLED AFTER EACH AGING TREATMENT
COERCIVE FORCE IN GILBERTS/C.M.
900 100 200 300 400 500 600
TREATMENTS IN DEG. C.
AGED FOR 24 HRS. AT EACH TEMP
ALL SAMPLES FURNACE COOLED FROM 900 °C.

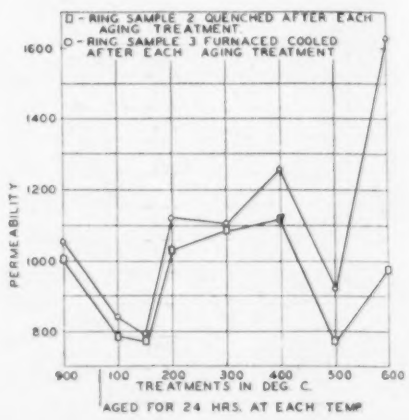

□ - RING SAMPLE 2 QUENCHED AFTER EACH AGING TREATMENT
○ - RING SAMPLE 3 FURNACED COOLED AFTER EACH AGING TREATMENT
PERMEABILITY
1600
1400
1200
1000
800
900 100 200 300 400 500 600
TREATMENTS IN DEG. C.
AGED FOR 24 HRS. AT EACH TEMP

Fig. 16—Change of Coercive Force During Aging of Metallic Arc Welds Slowly Cooled from 900 Degrees Cent. (1650 Degrees Fahr.) in Hydrogen.

Fig. 17—Change of Permeability During Aging of Metallic Arc Welds Slowly Cooled from 900 Degrees Cent. (1650 Degrees Fahr.) in Hydrogen.

meability are not consistent, although a similarity of the curves "as-quenched" and "as slowly cooled" is evident. These experiments were, therefore, repeated in a hydrogen atmosphere, using ring samples machined from pad H92. At the same time two bar samples were taken from arc welded pads "A" and "C" were included in this test. The results are plotted in Figs. 16 and 17. The sample 92-3 was furnace-cooled after the various aging treatments, sample 92-2 was water-quenched and the bar samples "A" and "C" were air-cooled. The curves of the coercive force of all samples show a second maximum at 400-500 degrees Cent., which is especially pronounced in the furnace-cooled ring sample and the air-cooled bar samples, while it is only very slight in the water-quenched ring sample. It was further found that the first maximum actually occurs at 150 degrees Cent. instead of 100 degrees Cent. The permeability curves show minimum values at 150 and 500 degrees Cent. due to the inverse relationship of coercive force and permeability.

The bar samples "A" and "C" were subjected twice to the same aging cycle in hydrogen atmosphere. After that the peak in coercive force at 100 degrees Cent. completely disappeared.

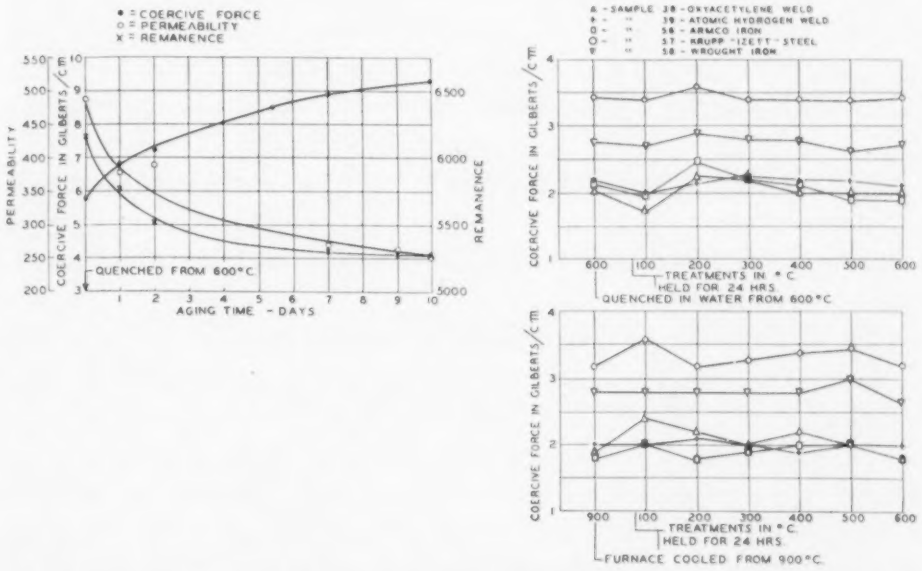

• = COERCIVE FORCE
○ = PERMEABILITY
x = REMANENCE
PERMEABILITY
COERCIVE FORCE IN GILBERTS/C.M.
REMANENCE
QUENCHED FROM 600°C.
AGING TIME - DAYS
A - SAMPLE 38 - OXYACETYLENE WELD
B - " 39 - ATOMIC HYDROGEN WELD
C - " 58 - ARMCO IRON
D - " 57 - KRUPP - IZETT - STEEL
E - " 58 - WROUGHT IRON
COERCIVE FORCE IN GILBERTS/C.M.
TREATMENTS IN °C.
HELD FOR 24 HRS.
QUENCHED IN WATER FROM 600°C.
COERCIVE FORCE IN GILBERTS/C.M.
TREATMENTS IN °C.
HELD FOR 24 HRS.
FURNACE COOLED FROM 900°C.

Fig. 18—Change of Magnetic Properties of a Metallic Arc Weld Quenched from 600 Degrees Cent. (1110 Degrees Fahr.) and Aged at Room Temperature.
Fig. 19—Change of Coercive Force After Various Treatments.

The bars "A" and "C" were now given the standard embrittlement treatment which should decrease the elongation to zero. It was found, however, that no increase in hardness occurred. The bars showed an extremely high ductility. The bars could be bent 180 degrees without showing cracks. The long continued hydrogen treatments apparently have removed so much nitrogen as to make the material insensible to heat embrittlement.

The magnetic changes during aging at room temperature, after quenching from 600 degrees Cent. (1110 degrees Fahr.), of an average arc weld No. 92 were studied in more detail and are recorded in Fig. 18. It is noteworthy that while the mechanical hardness reached its maximum after 2 or 3 days the coercive force or "magnetic hardness" is still rising after 16 days. Remanence and permeability change inversely with coercive force.

For a comparison, the changes of coercive force after various aging treatments are given for oxyacetylene welds, atomic hydrogen welds, ingot iron, wrought iron and Izett steel. The tests were made on bar samples in hydrogen atmosphere. The results are plotted

in Fig. 19. As seen from Fig. 19 the changes are very slight as compared with those encountered in arc welds. There is, however, one noticeable feature which was found first by Köster. After slowly cooling from 900 degrees Cent. (1650 degrees Fahr.) the samples H38, H56 and H57 show maximum coercive force after aging at 100 degrees Cent., while after quenching from 600 degrees Cent. (1110 degrees Fahr.) the maximum occurs at 200 degrees Cent.

Köster interpreted the maximum coercive force found at 100-150 degrees Cent. as being caused by the precipitation of nitrogen while he attributes the maximum at 200-250 degrees Cent. to the precipitation of carbon.

In metallic arc welds containing approximately 0.15 per cent N_2 the effect of such small amounts of carbon as 0.02 to 0.03 per cent is negligible as compared with that of nitrogen.

In comparing the mechanical hardness and the magnetic hardness of arc welds we find that the maximum mechanical hardness is obtained by aging at room temperature while the maximum coercive force occurs by aging at 100-150 degrees Cent., which shows that the influence of the arrangement and particle size is not the same for the two phenomena. The sharp increase in coercive force which results from aging at 100 degrees Cent. after quenching from 600 degrees Cent. (1110 degrees Fahr.) and the sharp drop at 200 degrees Cent. aging temperature show that there exist critical conditions for magnetic changes similar to our conception of a critical dispersion for maximum hardness.

Slow cooling from 900 degrees Cent. (1650 degrees Fahr.) holds only a portion of the nitrogen in solution, the bulk of it being precipitated. There is, however, sufficient nitrogen left dissolved to cause a noticeable peak at 100-150 degrees Cent. aging temperature. This indicates that however slowly a weld is cooled a certain amount of age hardening takes place which embrittles the metal and makes it difficult to obtain satisfactory ductility values.

The second maximum of coercive force at 400-500 degrees Cent. (750-930 degrees Fahr.) aging temperature which was found in some of the test samples after slowly cooling from 900 degrees Cent. (1650 degrees Fahr.) is of interest.

d. *Electrical Conductivity.* Variations of the electrical conductivity were used as another indication of solubility changes in

the iron-nitrogen system. In Table IX the effect of heat treatments as used in tensile testing on the electrical resistivity of arc and gas welds is illustrated.

Table IX
Resistivity Changes of Various Welds

Mark	Heat Treatment	Resistivity microhms/cm³
"A" Arc weld	As-received	13.14
	Quench 600 degrees Cent.	13.92
	Aged 10 days at room temperature	13.68
	Aged 1 day at 100 degrees Cent.	12.75
"C" Arc weld	As-received	12.30
	Quench 600 degrees Cent.	12.72
	Aged 10 days at room temperature	12.62
	Aged 1 day at 100 degrees Cent.	11.63
H38 Oxyacetylene weld	As-received	12.68
	Quench 600 degrees Cent.	12.72
	Aged 10 days	12.73
H39 Atomic hydrogen weld	As-received	13.32
	Quench 600 degrees Cent.	13.46
	Aged 10 days	13.42

As could be expected the changes are most pronounced in the two arc welds. The resistivity is increased greatly after quenching due to the increase of nitrogen held in solid solution while after aging at room temperature for 10 days the resistivity is decreased due to the precipitation of nitrogen in form of iron-nitrogen compounds. Remarkable is the decrease of resistivity of the arc welds after aging for one day at 100 degrees Cent., corresponding to the increase of coercive force at the same temperature.

In order to get a comparison with the results on coercive force after slowly cooling from 900 degrees Cent. (1650 degrees Fahr.) the same series of heat treatments was given to a number of arc welds. The arc welds included were: No. A, No. C, No. H46, No. H47 and No. H48. The cross section of the test specimens was 1/16 inch square by 12 inches long. The treatments were carried out in hydrogen atmosphere. The samples were air-cooled after each treatment. The results are collected in Table X.

The conductivity is increasing up to 100-200 degrees Cent. aging temperature. It drops then to a minimum which in some cases is reached at 300 degrees Cent., in others at 400 degrees Cent. At 500 and 600 degrees Cent. aging temperature a very pronounced rise in conductivity takes place.[14] The maximum at 100-200 degrees

[14]This rise of conductivity will be discussed later when more test data are available.

Table X
Resistivity Changes of Various Welds After Slowly Cooling

Mark	Slowly cooled from 900° C	Aged 24 hours at 100°C	200°C	300°C	400°C	500°C	600°C
	(Resistivity in Microhms per cubic centimeter)						
"A"	13.64	13.71	13.70	13.55	13.61	13.95	13.92
"C"-1	14.59	14.65	14.61	14.57	14.52	14.90	14.98
"C"-2	14.99	15.02	15.00	15.06	15.03	15.23	15.30
H46	12.63	12.70	12.72	12.60	12.48	12.87	13.24
H47-1	13.70	13.76	13.78	13.65	13.78	13.90	14.17
H47-2	13.80	13.96	13.95	13.80	13.78	14.12	14.42
H48-1	15.00	15.17	15.23	15.01	14.91	15.38	15.69
H48-2	14.82	14.97	15.00	14.90	14.92	15.12	15.47

Cent. is explained by the preciptation of the rest of the nitrogen kept in solid solution after slowly cooling while the minimum at 300-400 degrees Cent. is an indication that the nitrogen compounds are again taken up in solid solution.

e. *Structural Changes as Revealed by the Microscope.* The precipitation of iron-nitrogen compounds can be observed by means of the microscope. In the "as-received" state the arc welds show plates of nitrides arranged in Widmannstatten pattern as seen from Fig. 20. The needles are colored brown by etching in 2 per cent nital and darkened after an etch with hot alkaline solution of sodium picrate. After quenching from 600 degrees Cent. (1110 degrees Fahr.) the needles have disappeared, as can be seen from Fig. 21.[15] The particles precipitated during aging at room temperature are so highly dispersed that they cannot be seen under the microscope. After aging for 10 days at 100 degrees Cent. the structure corresponds to that shown in Fig. 22. The precipitate formed is of irregular shape with a tendency to form sharp cornered particles. After etching in sodium picrate the particles seem to consist chiefly of elongated plates arranged in a random manner. When aged for 10 days at 200 degrees Cent. the amount of precipitate increases somewhat and after 70 days at 200 degrees Cent. the groundmass is covered with the precipitate which again assumes the needle-like structure as is shown in Fig. 23. Aging at 300 degrees Cent. (570 degrees Fahr.) causes a precipitation of needles similar to that at 200 degrees Cent. as can be seen from Fig. 24. The number of needles appears to be smaller, but due to the nonhomogeneity of the welds it is difficult to photograph an average spot, as in some areas the amount of needles is large and in others small. It is, however,

[15] As etching reagent for the micrographs shown in this paper 2 per cent nital was used exclusively.

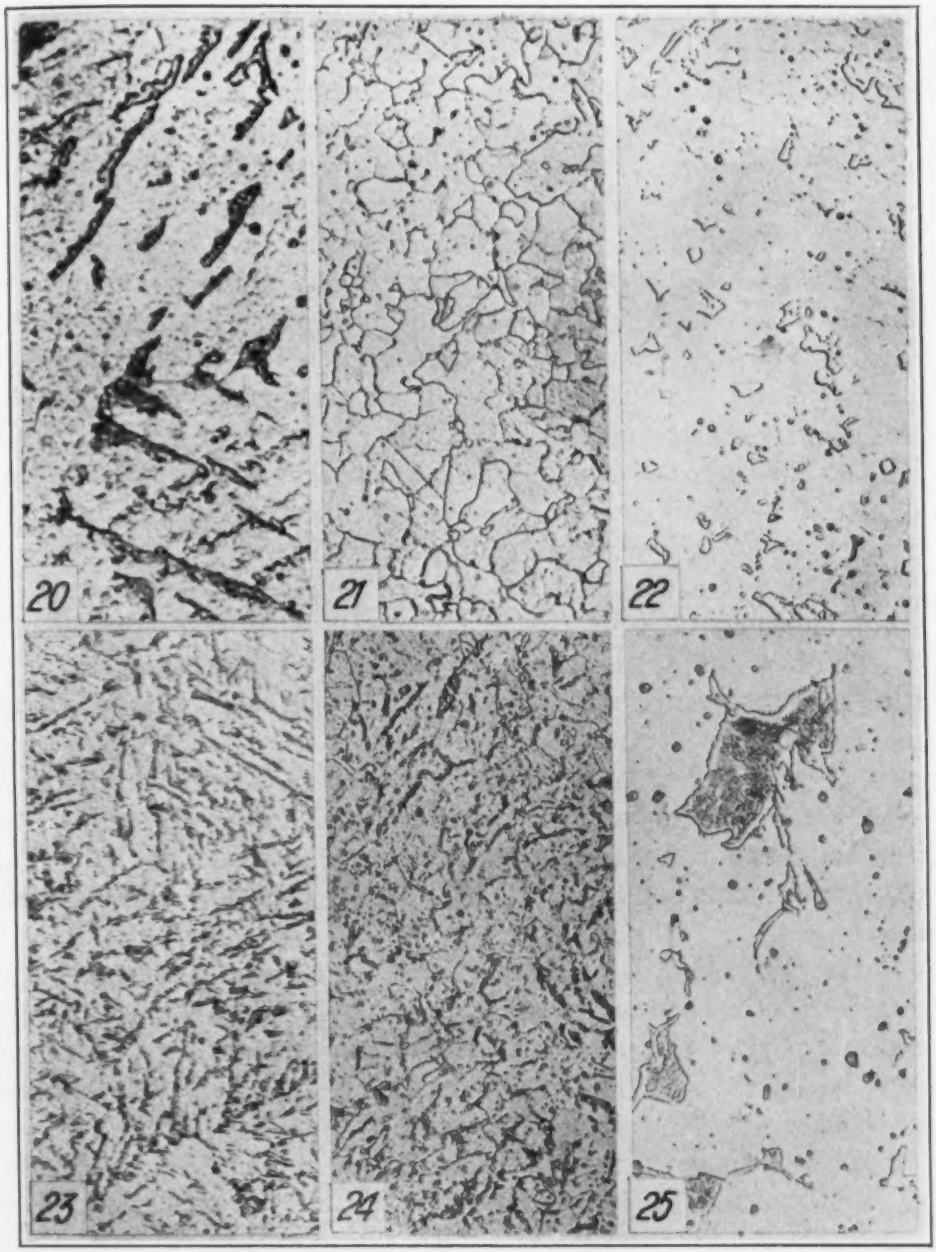


Fig. 20—Arc Weld "C" As-Received. × 1000.
Fig. 21—Arc Weld "C" As-Quenched from 600 Degrees Cent. (1110 Degrees Fahr.). × 500.
Fig. 22—Arc Weld "C" As-Aged for 10 Days at 100 Degrees Cent. × 500.
Fig. 23—Arc Weld "C" As-Aged for 70 Days at 200 Degrees Cent. ×500.
Fig. 24—Arc Weld "C" As-Aged for 20 Days at 300 Degrees Cent. (570 Degrees Fahr.). 500 ×.
Fig. 25—Arc Weld "C" Heated to 1000 Degrees Cent. (1830 Degrees Fahr.). Held for 2 Hours and the Furnace Cooled. × 500.
All Specimens Etched in 2 Per Cent. Nital.

to be expected that the number of needles will decrease at higher temperatures due to the fact that nitrogen goes into solution.

Heating for two hours at 1000 degrees Cent. (1830 degrees Fahr.) and slowly cooling entirely changes the appearance of the nitrogen precipitate. No needles are present, but a well-defined eutectoid is formed which apparently is Braunite.[16] It is shown in Fig. 25. Besides the eutectoid there appears a homogeneous constituent which usually surrounds small grains of the ferritic groundmass. This constituent is very likely the same chemically as the nitride precipitated in the form of needles. The constituent cannot be very hard, as could be seen from photomicrographs showing polishing scratches traversing it. It is not attacked by nital, but is darkened by sodium picrate. The constituent is made visible by a light etch with nital. It requires a much deeper etch to bring the grain boundaries out. By deep etching the ferrite around the constituent is badly corroded and sometimes gives the appearance of still another constituent.

With regard to the nature of the needles the authors are quite sure that they are caused by nitrogen. The characteristics of the needles, such as appearance after etching, sensitivity to heat treatments, darkening by etching with hot sodium picrate, are not characteristic of iron-oxygen compounds.[17] There is, of course, the possibility that a needle-like structure may be caused by a number of other elements but in the case of arc welds, nitrogen is undoubtedly the cause.

Oxyacetylene welds did not respond to the heat treatment applied to arc welds. The general appearance "as-received," "as-quenched" and "as aged at 100 degrees Cent." remains the same and is shown in Figs. 26 and 27. The grains in the "as-quenched" state are less susceptible to pitting than as received.

There is some material within the grain boundaries which has the appearance of cementite after etching in 2 per cent nital.

After cooling slowly from 1000 degrees Cent. a few nitride needles appear in oxyacetylene welds, indicating that more nitrogen is in the material than corresponding to the solubility limit at room temperature.

Atomic hydrogen welds in the "as-received" state show in places

[16] J. W. Owens, "Fundamentals of Welding," Cleveland, 1923.

[17] *Journal*, American Welding Society, Vol. 8, No. 9, 1929, p. 94.

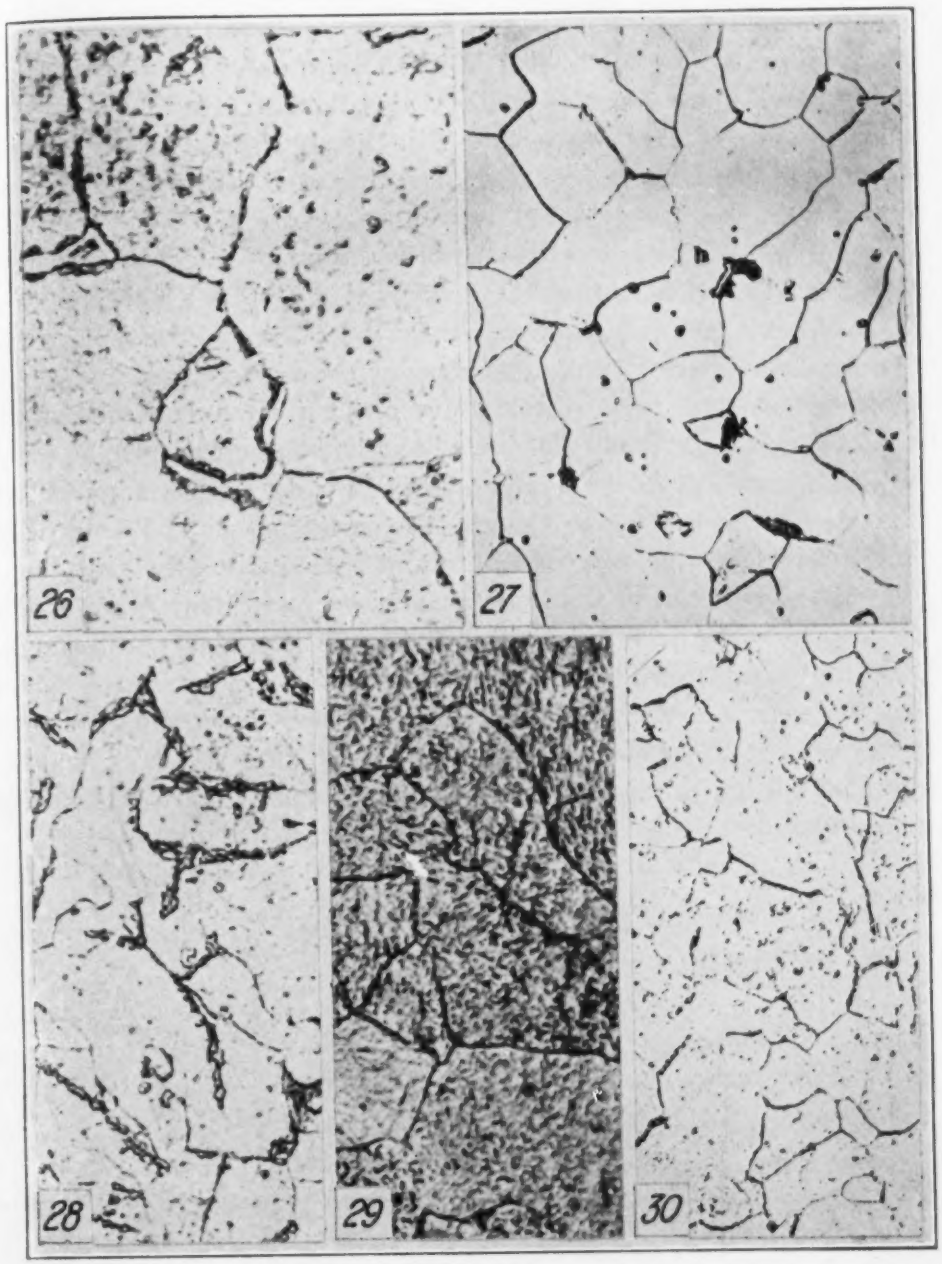


Fig. 26—Oxyacetylene Weld No. 38 As-Received. × 1000.
Fig. 27—Oxyacetylene Weld No. 38 As-Quenched from 600 Degrees Cent. (1110 Degrees Fahr.). × 250.
Fig. 28—Atomic Hydrogen Weld No. 39 As-Received. × 1000.
Fig. 29—Atomic Hydrogen Weld No. 39 As-Received. × 1000.
Fig. 30—Atomic Hydrogen Weld No. 39 As-Quenched from 600 Degrees Cent. (1110 Degrees Fahr.). × 500.

a needle-like structure (Fig. 28) resembling that of arc welds. The appearance of the needles, however, is quite different from those in

an arc weld. They seem to be broken up into small particles. Other places show grains subdivided into a large number of very fine particles which could be mistaken for etch figures (Fig. 29[18]). After quenching from 600 degrees Cent. a homogeneous grain structure appears as can be seen in Fig. 30. Aging at 100 degrees Cent. does not change the "as-quenched" structure.

An arc weld, oxyacetylene weld and atomic hydrogen weld were subjected to the McQuaid-Ehn carburizing test for eight hours at 900 degrees Cent. (1650 degrees Fahr.). All three welds showed an abnormal structure. While the edges of the oxyacetylene and atomic hydrogen weld showed very massive cementite the cementite of the arc weld was more finely distributed and had the appearance of coarse lamellar pearlite. In the atomic hydrogen and oxyacetylene weld the structure towards the core changes to pearlitic zones and areas while in the arc weld only free cementite and free ferrite are present.

The oxyacetylene weld contained very fine nitride needles; the atomic hydrogen weld had wider and more irregular needles and a very roughened groundmass. It is interesting to note that no typical needles were found in the arc weld, the nitrogen in the latter case appearing in the form of plates and very fine Braunite, as was observed before in the sample slowly cooled from 1000 degrees Cent.

Conclusions

To recapitulate the findings in this investigation the following points are made as a summary:

1. Arc welds contain 0.10 to 0.15 per cent nitrogen and can be considered as iron-nitrogen alloys. They show very pronounced aging effects after quenching from 600 degrees Cent. (1110 degrees Fahr.) and aging proceeds at room temperature.

2. The increase in hardness during aging depends upon the nitrogen content. This must be below approximately 0.05 per cent if satisfactory ductility and freedom from aging effects are to be obtained.

3. The tensile strength increases considerably during aging while the elongation, reduction of area and impact strength are decreased to practically zero.

4. Gas welds and atomic hydrogen welds are superior to arc welds made with bare wire, inasmuch as they show only a relatively

[18]The structure was brought out by a very light etch.

slight amount of aging embrittlement, which can be neglected for practical purposes.

5. The maximum magnetic aging of arc welds after a quench from 600 degrees Cent. (1110 degrees Fahr.) occurs at 100 degrees Cent. aging temperature. The coercive force is increased over 150 per cent. Remanence and permeability vary inversely with the coercive force.

6. After slowly cooling from 900 degrees Cent. (1650 degrees Fahr.) arc welds show pronounced magnetic aging at 100 degrees Cent. A certain amount of nitrogen is held in solution even by a slow rate of cooling, which is precipitated if the temperature is long maintained at 100 degrees Cent. This indicates the impossibility of obtaining ductile metal if the nitrogen content is in the neighborhood of 0.10 to 0.15 per cent.

7. The electrical resistivity decreases while the coercive force rises upon aging after quenching from 600 degrees Cent. (1110 degrees Fahr.).

8. The solution phenomena produce structural changes which can be detected microscopically. After quenching from 600 degrees Cent. (1110 degrees Fahr.) the precipitate formed at room temperature cannot be seen with the microscope. It becomes visible, however, when aged at 100 degrees Cent. The mechanical hardness occurring at room temperature is, therefore, caused by a submicroscopical dispersion, while the magnetic hardness is caused by a particle size of microscopical order.

9. Both arc welds and gas welds show extreme "abnormality" if subjected to the McQuaid-Ehn test.

Acknowledgments

The writers wish to acknowledge the generous cooperation of their colleagues at the Westinghouse Research Laboratories. The magnetic tests were carried out by C. F. Fusting, and the conductivity measurements by P. A. Ferguson, both of whom are particularly worthy of recognition. The writers are indebted to P. H. Brace, Manager of the Metallurgical Division of the Westinghouse Research Laboratories, for his encouragement and criticism concerning this work. Helpful suggestions were given by Dr. T. D. Yensen, Manager of the Magnetic Division, Westinghouse Research Laboratories.

The results are published with the approval of the Management of the Westinghouse Electric & Manufacturing Company as a contribution from their Research Laboratories.

DISCUSSION

Written Discussion: By F. T. Llewellyn, engineer, U. S. Steel Corporation, New York City.

The paper by Messrs. Hensel and Larsen is a valuable study on the effect of heat treatment on fusion welds, as well as their subsequent aging characteristics. Not being a metallurgist, I am not qualified to pronounce sentence on the comparative guilt of nitrides and oxides. Apparently they are both time-hardened sinners. However, everyday observation confirms the assurance that the important thing is to keep the fluid deposit away from AIR.

As far as I know little has been written on the effect of heat treatment on welds. In the December, 1926, issue of "Revue Universelle des Mines," Liege, Belgium, H. Dustin of the University of Brussels reports some tests on weld metal deposited by three brands of mild steel welding wire, identified as B, T and N. Brand B was plated with a 1¼ per cent nickel and covered with a braided asbestos fabric to confine thick slagging material. Brand T contained no nickel, but had a coating heavy enough to dispense with the covering fabric. Brand N had only a thin coating. The composition of the coatings is not reported. Weld metal deposited from the three brands by the ordinary arc process reacted to heat treatment as follows:

METAL B. When heated to 900 degrees Cent. (1650 degrees Fahr.) or higher, the hatched structure that is typical of weld metal deposits was replaced by ferrite, of fine or very fine grain according to the temperature reached and the speed of cooling. In general, each more or less vaguely defined grain turned into several smaller new grains. Quenching in water disclosed a mixture of troostite and martensite varying in proportions according to its temperature at time of quenching.

METAL T. When heated to 900 degrees Cent. (1650 degrees Fahr.) and cooled in air the typical structure remained unchanged. If heated to 1000 degrees Cent. (1830 degrees Fahr.) or higher, and cooled slowly in the furnace, the typical structure was replaced by fine-grained ferrite. If quenched in water from 900 degrees Cent. (1650 degrees Fahr.) ferrite in small tangled grains was secured, with a little badly formed pearlite interlaced in the joints. By drawing back after quenching the typical structure was restored.

METAL N. Even by maintenance for two hours at 1000 degrees Cent. (1830 degrees Fahr.) and cooling very slowly, the typical structure was not destroyed. The hatch marks merely became a little less numerous. If quenched and drawn back they were restored.

Professor Dustin concluded that it would be useless to try to anneal metals T or N, and that a treatment sufficient to change the typical structure of metal B would increase resilience only about 12 to 15 per cent, and reduce hardness only about 10 to 12 per cent, which usually would not be sufficient to justify the expense of an annealing process.

With regard to age-hardening, my attention has been called to some ordinary commercial arc welded joints, made with bare wire which, shortly after being deposited, successfully met a practical impact test in the shape of severe blows from a sledge hammer. Some months later, while the members were being installed, some of the welds fractured under much less severe impact. In this case the trouble was easily taken care of by re-arranging the location of the welds so as to better resist flexure. The occurrence raises a question as to the possible age-hardening of welds that have received no heat treatment.

The officials of the laboratory with which Messrs. Hensel and Larsen are connected are to be complimented on the candid manner in which they have permitted the conclusions to be stated.

Written Discussion: By J. C. Lincoln, Lincoln Electric Co., Cleveland.

I have read Messrs. Hensel and Larsen's paper with a great deal of interest and congratulate them on the work that they have done. It has always seemed to me that the presence of gas in steel that has been welded is one of the causes of its somewhat peculiar action and then until gas analysis is carried to a greater extent than it ordinarily is at the present time, that explanation of some phenomena will be impossible.

Some 6 or 8 years ago in working on this same problem of getting brittleness out of arc welds, the question of what made arc welds brittle arose very prominently. At that time and at the present time it would seem to me that it was more reasonable to assume that the brittleness was caused by the action of oxide on the weld metal rather than nitrides.

The fundamental fact is very apparent that in the case of metallic arc welds, most of the carbon and most of the manganese is oxidized in going across the arc. In the ordinary metallic electrode the percentage of manganese is from 0.4 to 0.6 per cent and the carbon about 0.15 per cent, or the two together approximately 0.66 per cent. It seems to me very evident that if most of the 0.66 per cent of carbon and manganese are oxidized out in crossing the arc, that a very large amount of iron is oxidized at the same time. This becomes evident when we realize that there is approximately 150 times as much iron in the electrode as there is carbon and manganese together. The theory that I have worked on has been that a considerable amount of iron was oxidized in its passage across the arc and this iron oxide was dissolved in the remaining metal, producing the effects which are so fully described in the paper.

However, from a practical standpoint, it makes no difference whether the brittleness is caused by the action of the oxygen or by the action of the nitrogen on the electrode material as it crosses the arc. Many thousands of experiments have indicated that the only way to get rid of the brittleness is to produce a ductile weld and to do this both oxygen and nitrogen have to be excluded from the arc and an appreciable amount of hydrogen introduced. When this is done, the brittleness which is inherent in ordinary bare wire welds is overcome and the ductility approaches that of the parent metal.

There is another effect which occurs with ordinary bare wire welds which is not mentioned in the paper, which may be of interest. Ten or 15 years ago we made a cage for holding laminations to go into an annealing furnace. This cage was welded up with bare wire and used. Within a comparatively small

number of heats, cracks developed in the welds and shortly these cracks extended clear through the weld. We always speak of this action by saying that the weld "rotted." For the purpose in question this was a serious difficulty with bare wire metallic arc welds. Later experiments with ductile welds showed that the weld metal which was ductile was free from the difficulty mentioned above. One particular sample tested, was welded with metal which was ductile, was heated to 1600 degrees Fahr. and cooled about 50 times. At the end of this time, the weld showed no more deterioration than the parent metal.

It would be very instructive to find out what causes cracks in the bare wire metallic arc weld on repeated heating and cooling, but the important practical question was to produce a metal which did not act that way.

Judging from a number of the tables and curves in Messrs. Hensel and Larsen's paper, I am certain that if their tests had been made on welds which were made with heavily covered electrode which could produce ductile metal in the weld that the results which they have outlined would have been very different and would closely approach the results of the parent metal.

Written Discussion: By Dr. W. Köster of Vereinigte Stahlwerk A. G. Forschungsinstitut, Dortmund, Germany.

I congratulate Messrs. Hensel and Larsen for their excellent work on the importance of nitrogen in influencing the properties of weld metal. Their results have a special interest for me, since they have made use of the facts about the influence of nitrogen in steel, which I described in my paper, as applied to so technically important a process as welding. They show impressively how the results of investigations which were first carried out from a more theoretical point of view can also furnish important data on quality in testing materials. I am especially pleased to state that the results which Hensel and Larsen obtained on samples of weld metal agree in all testing methods with mine, which were obtained on nitrided steel samples and nitrogen bearing ingot iron. This agreement even extends to details. Thus it follows that, in general, when a substance is precipitated from a supersaturated solid solution, the remanence, and at the same time the coercive force, rise. An exception is the precipitation of nitrogen, where the remanence increases at first 200 degrees, while the maximum value of the coercive force remains around 100 degrees. The authors further found, in agreement with me, that the hardness of steel containing large amounts of nitrogen was raised after quenching from 500 degrees or above and that the elongation was greatly reduced. These results have not been studied to a very great extent by other investigators in this country.

I attach no great importance to the secondary maximum in aging. My opinion is that it is caused by the partial precipitation of nitrogen during slow cooling. After this treatment, the value usually varies greatly according to the stimulation of the still undissolved nitride particles or other inclusions given by the nitrogen content. On the other hand, the curve of the change of coercive force of the quenched specimen runs smoothly. It should also not be left out of account that the ratio in Fig. 16 is considerably larger than in Fig. 13, and that the highest and the lowest values are separated by only 1 or 2 gauss. These differences are, however, explained by the distribution of nitrogen, to which

the coercive force is extraordinarily sensitive. With low nitrogen content, up to about 0.03 per cent, the increase of coercive force can be used for the quantitative determination of nitrogen, for the coercive force rises proportionally to the amount of precipitated nitrogen. 0.01 per cent of nitrogen precipitated at about 100 degrees raises the coercive force about 3.2 gauss. With higher nitrogen content, such as is present in welded joints, however, this is no longer the case. The proportionality ceases to exist. The coercive force at 0.15 per cent nitrogen should increase about 45 gauss, while it actually increases only about 17 gauss.

The importance of the present investigation for judging the welding process is beyond doubt, and will become more and more apparent with further study of the discussed questions. Without doubt, failure of welded joints is caused by nitrogen brittleness. One can conclude, when this occurs, that a weld was made with a thin electrode on a thick plate so that in the resultant rapid cooling a large amount of nitrogen remained dissolved. However, this condition is only occasionally met with, so that, on an average, good elongation and tensile properties are obtained even in the electric arc welded joint.

Written Discussion: By A. Nadai, mechanics' division, research laboratories, Westinghouse Electric and Manufacturing Company, East Pittsburgh.

The age hardening phenomena in metallic alloys have recently attracted, not only the metallurgists, but also the attention of the mechanical engineers for various reasons. It is extraordinarily interesting to see the progress made in recent years in this special field of metallurgical research. The great effects of minute quantities of nitrogen which may be dissolved in steel or, according to various conditions, be again precipitated out of it, have attracted the writer's attention, particularly in connection with the formation of the so-called strain or flow figures (Lüders lines) so characteristic for mild steel. Everyone who has had an occasion in former years to investigate these figures appearing on steel specimens after the yield point has been exceeded and who has tried to use the etching method by Dr. A. Fry, Essen, as suggested some ten years ago in "Kruppsche Monatshefte" for demonstrating or developing these interesting figures on strained specimens of steel was frequently greatly disappointed in finding how differently steel specimens tested under seemingly quite similiar conditions (having the same chemical analysis, tested under the same states of strain and using the same etching solution and heat treatment) were responding to the etching treatment. The writer, being much interested in the development of these strain figures, remembers that on account of the difficulties encountered in obtaining satisfactory etchings of them, called on a well-known metallurgist abroad. The writer had an instinctive feeling rather than one based on rational reasons that some minute quantities of a material dissolved or contained in the steel which has escaped attention, until now, might have had something to do with the darkening of the strain figures. It has also been observed, for example, that the strain figures could be more distinctly seen in the inner portion of the bar's cross-section. This was brought together with the segregations in the ingot from which the bars originated. The writer did not succeed, however, to interest the metallurigst in question and in obtaining,

as he suggested, a chemical analysis of the black precipitation causing the strain figures.

It is encouraging to see today how conditions have quite changed, since by the work of Köster and Hensel the nitrogen content in steel has been brought together with the causes of the so-called magnetic aging and also with the possibility of etching the strain figures. On this question further work is in progress and it can be hoped that it may lead, with the combined efforts of the metallurgists and the mechanical engineers, to an elimination of those difficulties mentioned above.

Another point of interest which may be mentioned here at least with some few words is a possible connection of the age hardening phenomenon as carefully studied by Messrs. Hensel and Larsen in this present paper on the weld metal specimens with such a phenomenon as that of the creep of metals. Messrs. Hensel and Larsen have conclusively demonstrated the slow hardening of steel with a subsequent softening under circumstances while kept under a moderately elevated temperature and observed during comparatively long periods of time. It will be pointed out elsewhere by P. G. McVetty that while observing alloy steel bars exposed to long time tests under tensile loads and elevated temperatures that the observed creep rates may be affected by strain hardening as well as by a subsequent softening, which latter may show up in its effects only after long periods of time, depending on conditions. The interesting observations of Hensel and Larsen, showing still slower changes of the Brinell hardness of steel weld metal during several hundred hours after keeping the specimens exposed to slightly elevated temperatures, may be of importance in connection with creep of steels. Certain of his results may prove valuable and useful in stimulating further investigations about factors having an influence on the creep phenomenon of metals.

Written Discussion: By Gilbert E. Doan, associate professor of physical metallurgy, Lehigh University, Bethlehem, Pa.

It has always been surprising that arc welds, being nearly carbon-free and low in other alloy elements, were so hard and strong, whereas, nearly pure iron should be soft. Lately we began to suspect that the rapid cooling of the weld, although not producing a hardening through the carbon, might nevertheless set the stage for a subsequent aging participation. These views were set forth by the author at the Annual Lehigh Welding Symposium this year. The present authors have here made an important contribution to the metallurgy of arc welding.

From the account published in *Metal Progress* it does not, however, seem proven that it is necessarily nitrogen which causes the aging. The loss of nitrogen when the specimen is heated in hydrogen for four days at 1000 degrees Cent. (1830 degrees Fahr.) is found to be accompanied by a loss of age hardening properties. May there not be a loss of carbon or other elements as well as nitrogen and may not one of the other elements be the one really responsible for the aging? A. A. Bates has found this to be the case in extra soft Bessemer steels of a similar carbon content.

In 1929, P. P. Alexander of the Thomson Research Laboratories, General Electric Company, conducted a careful series of welds in pure gases and pub-

lished them in the American Welding Society *Journal* for September, 1929. Mr. Alexander found that these same needles, shown in the present paper, are present in welds made in gases not containing nitrogen. For example, welds made in an atmosphere of argon, of carbon dioxide, or of carbon monoxide, or even in mixtures of argon and oxygen, none of which gases contained nitrogen, all showed considerable amounts of such needles. On the other hand, he found that welds made in pure argon or nitrogen were perfectly free from needles. Naturally this discovery led him to the conclusion that it must be oxygen, and not nitrogen, which produces the needles, and that they are in all probability an iron-iron oxide eutectic.

If any of the samples were annealed in air for a long time, they invariably showed the characteristic needles also, no matter in what atmosphere the welding had been done. Because of this careful study it might be well to raise the question whether the needles shown by the present authors necessarily are nitride needles and also whether nitrogen is responsible for the age hardening of these welds.

Aside from this question, the authors certainly have shown that welds do age harden, and what is likewise important, that annealing at 200 or 300 degrees Cent. will soften such welds and increase their ductility. At some part of most welds the cooling rate is probably rapid enough to cause some subsequent age hardening. Although this is not brought out in the author's Hardness-Time curves of quenched welds, it seems almost a necessary sequence of the steep temperature gradient which exists near the arc. Annealing would be expected to remove the brittleness in these rapidly cooled zones, and thus to improve the quality of the welded joint.

Written Discussion: By P. P. Alexander, Thomson research laboratory, General Electric Company, Lynn, Mass.

The authors are to be congratulated upon the contribution they have made to the rational study of metallurgy of fusion weld metal. The amount of work which has been necessary in order to complete such a paper, is, without doubt, enormous.

Although I may differ with the authors on certain points, yet I am of the opinion that this valuable paper sheds a new light on one of the most important questions of the metallurgy of fusion welds.

Due to extremely high temperatures at which the welding operations are carried out, the influence of the gases surrounding the welding arc is so great, that no effort should be spared in the investigation of their effect. A great amount of research data published on the subject of influence of nitrogen or oxygen on iron, allows us to form a precise idea of what can be expected from a given alloy containing a certain percentage of either of those elements.

The experiments with the nitrided electrolytic iron establish that nitrogen increases tensile strength, reduces somewhat the elongation and produces precipitation hardness. It has been established also that iron-oxygen alloys have a hardness somewhat higher than pure iron, that they possess lower elongation and are very brittle under impact tests.

Metallographic investigations also establish what percentage of nitrogen is detectable by the microscope after suitable heat treatment. We know the various

metallographic formations in which iron nitride may be present. As has been shown in a paper recently published by Dr. Frank W. Scott, we can even predict the physical properties of steel containing a given percentage of nitrogen and by using a mathematical formula, Dr. Scott is able to calculate either tensile strength or elongation of the nitrided steel. Yet in spite of the abundance of data already obtained, it cannot be applied to fusion welds without further experimental confirmation, since the conditions here are quite different from those under which that data was obtained.

Fusion welds are made at temperatures very much higher than those obtainable in the metallurgical furnaces, and both oxygen and nitrogen are present in an atmosphere surrounding the arc. The result is that the weld metal is contaminated to a high degree with nitrides as well as oxides. Furthermore, it usually contains a certain amount of carbon, the influence of which is by no means negligible. Other elements, such as manganese, are usually present in the alloy. Therefore, in dealing with the fusion welds, we cannot consider the weld metal as a pure iron-nitrogen or iron-oxygen alloy. It is a complex alloy produced under very special conditions of temperature, rapid quenching and often containing a considerable amount of nonmetallic inclusions and blow holes. It is clear, therefore, that without further experimentation, it is difficult to predict the behavior of the fusion weld from the data obtained with the pure alloys prepared under the best laboratory conditions. Therefore, the work of the authors of this paper is of special value, since, in their investigation, they dealt not with electrolytic iron nitrided by ammonia, but with the fusion welds produced under conditions similar to that met in practice where all additional factors influence the results. The data obtained by the authors supplies a method of ascertaining the quality of the fusion welds. They should be congratulated for their attempt to give definite figures for nitrogen content in the weld metal which can be used as an indicator of the quality of the weld. By means of chemical analysis we shall now be able to predict the behavior of a produced weld. It may be stated, therefore, that the results of the work of the authors will be of great value to the fusion welding industry.

Referring now, not to the concrete data obtained by the authors, but to the interpretation of that data, I may state that to my mind a somewhat modified explanation could be given to the causes producing such results. The analysis of the arc welds experimented with by the authors shows that besides nitrogen, it contains a large amount of oxygen and an appreciable amount of carbon. Therefore, in discussing the properties of such welds, we may attribute the modification in the physical properties not only to the influence of nitrogen but also to oxygen and carbon.

The authors, for instance, believe that the precipitation hardness of the arc welds is due to nitrogen. The data presented by the authors is quite convincing and shows that in the special conditions in which the experiments were conducted, the influence of nitrogen was preponderant. However, it should be pointed out that in general practice, the weld metal after solidification is cooled very rapidly, which is equivalent to quenching, not from 600 degrees Cent. (1110 degrees Fahr.), but from considerably higher temperatures. In such an event, the influence of small amounts of carbon always present in the welds

will exert also a very marked effect. In fact, carbon alone could be entirely responsible under such conditions in producing the precipitation hardness. This, of course, can be predicted by mere examination of the equilibrium diagrams of iron-nitrogen and iron-carbon alloys. The lower parts of the left side of those diagrams are very similar, which show that solubility of either nitrogen or carbon in alpha iron at room temperature is much lower than at 600 or 700 degrees Cent. (1110 or 1290 degrees Fahr.).

The available experimental data confirms the expectation of the similar behavior of carbon and nitrogen in producing the precipitation hardness. It may be noted also that in the September issue of *Metal Progress*, Dr. E. W. Ehn gives further experimental data which reconfirms previous tests. In discussing the precipitation hardness observed in low carbon steels, Dr. Ehn gives an example of a sample containing 0.028 per cent of carbon and a normal amount of nitrogen which has been quenched from a temperature of 660 degrees Cent. (1220 degrees Fahr.). After nine days the hardness increased from 102 to 191 Brinell. With the exception of nitrogen this sample has an identical chemical analysis with the sample experimented with by the authors and indicated as arc weld "C".

This indicates that in practical applications, both nitrogen and carbon will be responsible for age hardening of the welds. Considering now the impact resistance of the welds, we should take into consideration the influence of not only nitrogen but also oxygen, since the weld metal in open arc welds is highly oxidized.

In the case of the atomic hydrogen and oxyacetylene welds aged for eight days, the results of impact tests were given as 79 foot-pounds for atomic hydrogen welds and only 8.3 foot-pounds for oxyacetylene welds. And yet, the chemical analysis shows that the atomic hydrogen welds contain more nitrogen than those produced with oxyacetylene by the oxyacetylene process.

Considering now the extremely small elongation of the weld metal produced by electric arc, we may again question whether it is due to nitrogen alone. The data published by Strauss as early as 1914 on the tensile strength and elongation of nitrided low carbon steel containing 0.07 per cent carbon, indicated that with the increase of nitrogen, the tensile strength increased and the elongation decreased slightly, yet even with the nitrogen content of 0.16 per cent, which is that found in most of the arc welds, the elongation was still 22.5 per cent. In the recently published paper by Dr. E. W. Ehn quoted above, he gives an example of a specimen containing 0.50 per cent nitrogen quenched from 550 degrees Cent. and tempered at 250 degrees Cent. which gave an elongation of 30 and reduction of area, 80 per cent.

To my mind, these facts indicate that in welds produced under usual conditions in practical work, the reduced elongation, low impact resistance, and precipitation hardness should be attributed to the influence not only of nitrogen but also of oxygen and carbon. The same conclusions apply to the change in the electrical and magnetic properties of the fusion welds since it has been established quite definitely that oxygen has a very great effect on those properties of steel.

With respect to structural changes and metallographic aspects of the welds

quoted by the authors, I noticed that all the welds after carburization by the McQuaid-Ehn method give highly abnormal steel which is an unmistakable indication of their contamination with oxygen. With respect to the needle-like formations found by the authors in arc as well as atomic hydrogen and gas welds and usually indentified by the great majority of investigators as iron nitrides, their presence or absence does not give definite information with respect to the quality of the fusion welds. It is known that they can be present in electrolytic nitrided iron containing as low as 0.05 per cent nitrogen. On the other hand, in the presence of carbon these formations will not be apparent even if the quantity of nitrogen in steel be as high as 0.15 per cent.

In view of the fact that the embrittling effect of nitrogen increases with carbon content, this coincidence is most unfortunate. As F. W. Scott has indicated, zero elongation in low carbon steel of 0.06 per cent of carbon will be caused by 0.165 per cent nitrogen, yet in eutectoid steel 0.01 per cent of nitrogen is sufficient to reduce the elongation to zero.

These two considerations, that nitrogen is not revealed by metallographic methods in the carbon steels and that its bad effect is especially pronounced in those particular steels, indicate that metallographic method of ascertaining the quality of the weld can be thought of as not nearly as valuable as the chemical analysis, used by the authors in their investigation.

I may mention also that in my investigations of the welds produced in pure carbon monoxide, I found the presence of the needle-like formations similar to those found in usual arc welds. This leads me to believe that these formations may be caused under different conditions by different elements. That is, by nitrogen in nitrided steel and by oxygen or the combination of oxygen with other elements in welds produced in pure carbon monoxide.

In conclusion, I wish to state that in spite of the difference of opinion which I hold in interpreting some of the results obtained by the authors, I am of the opinion that the concrete data obtained by the authors stands without challenge and will constitute a most valuable contribution to the knowledge of the metallurgy of the fusion welds.

Authors' Closure

The authors wish to thank the various individuals taking part in the discussion of their paper. They are particularly pleased with the more or less general agreement with the facts reported in their paper. Data mentioned by Messrs. Lincoln, Alexander and Llewellyn show the practical importance of room temperature aging and of heat embrittlement of bare wire welds. Doubts seem to exist only as far as interpretation goes. Likely a number of factors may contribute to the phenomena observed in those bare wire welds. The results, however, are in such perfect agreement with data observed by Köster on the precipitation of nitrogen in steel as mentioned in our paper and in Dr. Köster's discussion that the authors are convinced that nitrogen is the predominant factor. Research, however, is under way to investigate to what degree carbon and oxygen are responsible for the results of our paper. Similar research is being undertaken by Dr. G. E. Doan.

INFLUENCE OF GRAIN SIZE ON THE PROPERTIES AND CORROSION RESISTANCE OF THE 18-8 IRON-CHROMIUM-NICKEL ALLOY FOR ELEVATED TEMPERATURE SERVICE

By H. D. Newell

Abstract

The use of the 18-8 alloy steel, for elevated temperature service involving stress and corrosion, makes it of extreme importance to have the alloy part in its best condition for maintenance of ductility and corrosion resistance.

In this paper, the author shows, by means of short time high temperature tests and by certain corrosion tests after heating within the carbide precipitation range, that the grain size of the alloy has an important influence on ductility at elevated temperature and on maintenance of corrosion resistant properties.

The preliminary part of the paper shows the influence of initial heat treatment on the grain size of the alloy and the main portion deals with the physical properties of two carbon grades of the alloy at temperatures within the range 800 to 1700 degrees Fahr. (425 to 925 degrees Cent.) inclusive. Corrosion tests, made after reheating at a selected temperature of 1200 degrees Fahr. (650 degrees Cent.) show an important relationship between grain size and ability to resist the intergranular type of corrosion attack. The "grain boundary extent" available to the precipitated carbides, as fixed by grain size, together with carbon content, control the corrosion behavior of the alloy after heating.

Conclusions are drawn that the optimum heat treatment for ductility and corrosion resistance for low temperature service is not the optimum for these properties at temperatures within the carbide precipitation range. Restriction of carbon content and the maintenance of a small grain size by limiting the temperature employed in heat treatment, produce the most satisfactory condition for ductility at elevated temperature and maintenance of corrosion resistant properties.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, H. D. Newell, is a member of the society. He is chief metallurgist with the Babcock and Wilcox Tube Co., Beaver Falls, Pa. Manuscript received May 20, 1931.

Introduction

WITHIN the group of nonrusting chromium-nickel steels originating with Professor Doctor Benno Strauss,[1] the alloy steel containing approximately 18 per cent chromium and 8 per cent nickel has come into extended use in this country during the past three or four years. Being available in all forms and with admirable properties and corrosion resistance, it is now widely used in the chemical industry, in the food industry, in the manufacture of paper, for structural and decorative purposes, and as an engineering material for elevated temperature service in both the refining industry and in steam power plants.

In the development of the austenitic chromium-nickel steels, Dr. Strauss discovered that ductility, nonmagnetic qualities and corrosion resistance were developed to the greatest extent by application of heat treatment after working, forming or fabricating. This heat treatment, which Strauss patented,[2] consisted of heating to a high temperature and subsequently quenching in water or otherwise quickly cooling to preserve the homogeneous austenitic structure and to retain the carbon in solution.

At that time, the melting, production and application of the chromium-nickel steels were not so far advanced as they are at present, and the alloys contained a substantially greater carbon content than is now generally used. The temperatures specified for heat treatment were necessarily high, due to the high recrystallization temperatures of the alloys and because the solubility of the carbon (carbides) increases with rise in temperature.

In many present applications of these chromium-nickel steels, maximum benefit to certain properties is secured by cooling from temperatures sufficiently high to cause complete solution of the carbides, but in the case of very low carbon alloys, not too high to incur heating within the "austenite-delta" field. It is generally viewed that maximum ductility and corrosion resistance is produced in the 18-8 type alloy steel by quickly cooling from temperatures within the range 2000 to 2200 degrees Fahr.[3] (1095 to 1205 degrees Cent.).

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[1]B. Strauss, "Non-Rusting Chromium-Nickel Steels." *Proceedings,* American Society for Testing Materials. Vol. 24—Part II, 1924, p. 208.

[2]Benno Strauss, U. S. Patent No. 1,404,908 (January 31, 1922).

[3]See National Metals Handbook, 1930 Edition, American Society for Steel Treating, "Stainless Steels" by Owen K. Parmiter, p. 254.

Low and High Temperature Service Conditions

As is well known, the austenitic structure of 18-8 produced by heat treatment is not stable under all conditions. Cold work may develop ferrite, and exposure to certain elevated temperatures may also induce ferrite separation or permit carbide precipitation. The extent of these changes in structure is dependent on the particular composition of the alloy and the thermal or mechanical treatment received.

For low temperature service involving various types of corrosion, in which the author has in mind particularly corrosion encountered in aqueous solutions of acids and salts at relatively low temperatures, or ability to be cold formed wherein ductility is of importance, heat treated 18-8 alloy is employed to the greatest advantage. This class of service demands no particular consideration of carbon content (providing it is in solution) or of grain size resulting from high temperature heat treatment. The 18 per cent chromium, 8 per cent nickel alloy containing under 0.16 per cent carbon has commonly been employed in the heat treated state below the temperatures at which carbide precipitation occurs and has not been used to any extent for high temperature service because of changes in properties such as loss in corrosion resistance, impact, ductility and increase in hardness and yield point due to precipitation of carbide particles at elevated temperatures.

For elevated temperature service, i.e., coming near or within the temperature range in which carbide precipitation will occur on heating, a low carbon content 18-8 alloy has been used to the greatest extent. Such material usually contains a maximum of 0.07 per cent carbon so that detrimental changes in physical properties and loss in corrosion resistance due to carbide precipitation are restricted to a minimum.

A considerable amount of 18-8 alloy has been used in the form of seamless tubes involving the handling of corrosive gases and liquids at elevated temperatures under both high and low pressures. The condition of the alloy with respect to maintenance of corrosion resistance and physical properties is of importance in ensuring satisfactory service. In elevated temperature service, especially in the oil refining industry,[4] the failure of an 18-8 alloy tube, due to overheating,

[4] H. D. Newell, "The 18-8 Iron-Chromium-Nickel Alloy with Particular Reference to its Characteristics for Cracking Coil Service," American Petroleum Institute, Paper for the Spring Meeting, St. Louis, Mo., April 16, 1931.

occurs without a warning bulge and fracture results without appreciable ductility. The alleviation of this condition, by increasing the ductility of the alloy through the temperature range in which failure is likely to occur, is of extreme importance to users of the material in such industries where failure of a part represents a hazard.

Purpose of Investigation

Having this latter class of service in mind, the object of this investigation was to determine the effect of grain size on the ductility of the 18-8 alloy through a certain range of temperature and to find out the relationship of grain size to corrosion resistance after heating to a temperature sufficient for the occurrence of carbide precipitation.

The investigation is divided into two parts, the first part includes experiments showing the influence of temperature and time on the grain size resulting from initial heat treatment of the alloy. The second part deals with physical tests at elevated temperature, corrosion tests after prolonged heating and the relationship of grain size to carbide precipitation and its subsequent effect on the behavior of the alloy toward intergranular corrosion.

Part I

Influence of Heat Treatment on Grain Size

The removal of strain resulting from cold work, or hot work below the recrystallization temperature, is accomplished by heating the 18-8 alloy to a high temperature. The grain size resulting from such heat treatment is influenced by the temperature employed and by time at temperature. In common with many other metals and alloys,[5] the higher the temperature to which 18-8 alloy is heated above its recrystallization temperature, the greater will be the resulting grain size. Grain growth is also affected by time at temperature and the longer the alloy is exposed, the greater will be the grain size. With sufficient time, equilibrium grain size is probably reached for each temperature so that further heating at such temperature produces no further growth.

In connection with the influence of time in heat treating, an ex-

[5]Jeffries and Archer, "The Science of Metals," 1st Edition, 1924, p. 85. McGraw Hill Book Company, Inc.

periment was made using a 0.400-inch square cold drawn, unannealed rod of the following composition:

Carbon	0.08 per cent	Silicon	0.46 per cent
Manganese	0.38 per cent	Chromium	18.25 per cent
Sulphur	0.014 per cent	Nickel	8.10 per cent
Phosphorus	0.019 per cent		

Sections of this rod of equivalent size were heated in a carborundum rod resistance furnace for time periods of ten minutes and three hours at temperatures of 1850 degrees Fahr. (1010 degrees Cent.), 2000 degrees Fahr. (1095 degrees Cent.) and 2150 degrees Fahr. (1180 degrees Cent.) respectively. After water quenching, a microscopic examination of grain size was made. Fig. 1 shows the average grain sizes found for these treatments together with the structure of the original rod.

The reagent used in the author's laboratory for etching heat treated 18-8 alloys consists of 25 parts of concentrated hydrochloric acid and 5 parts of a 10-per cent solution of chromic acid. This etch originally consisted of aqua-regia containing chromic acid and for that reason was termed "chrome-regia." It has been in successful use for several years, and, although now used without the nitric acid, it is still termed chrome-regia. The function of the chromic acid is to slow up the action of the hydrochloric acid to prevent pitting and staining. For cold-worked materials, the amount of chromic acid should be increased to 50 parts of 10-per cent chromic acid which gives a very gentle etching medium.

The second experiment consisted of heating specimens of 7/8-inch diameter, hot-rolled rod at various temperatures from 1800 to 2400 degrees Fahr. (980 to 1315 degrees Cent.) inclusive. In this case, the time element was held constant and the heat treating temperature increased 100 degrees Fahr. (38 degrees Cent.) for each set of specimens. After 45 minutes at temperature, they were quenched in water at 70 degrees Fahr., and examined for grain size. The average size found is shown in Fig. 2.

Composition of the material used was:

	Per Cent
Carbon	0.056
Manganese	0.35
Silicon	0.34
Chromium	17.76
Nickel	9.06

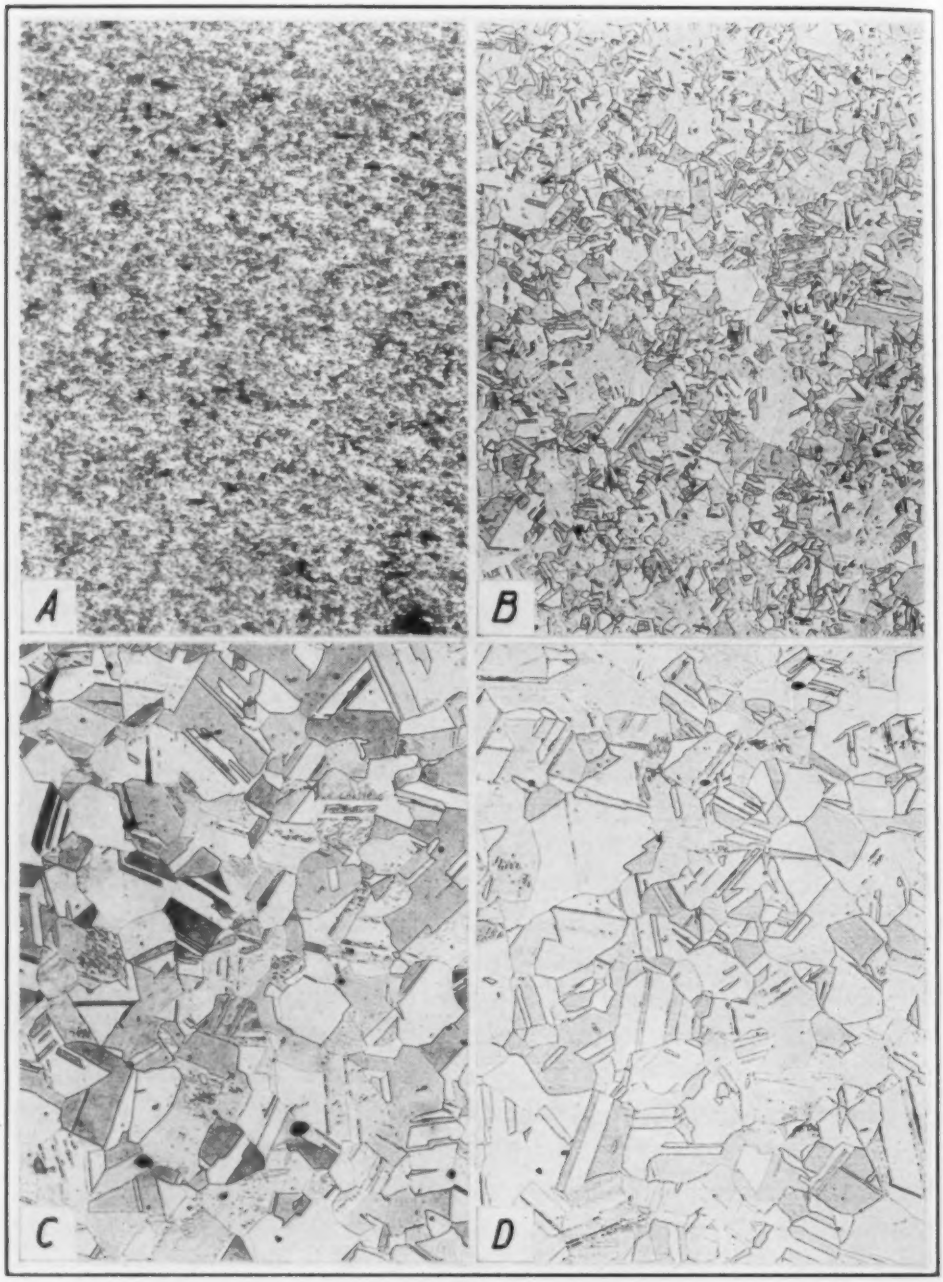


Fig. 1—Photomicrographs of Grain Size of 0.08 Per Cent Carbon "18-8" Alloy in the Cold Drawn State and after Various Heat Treatments. Etched with "Chrome-regia." × 100.

A—Cold Drawn, unheated, Brinell 317.
B—10 Minutes at 1850 degrees Fahr., quenched, Brinell 165.
C—3 Hours at 1850 degrees Fahr., quenched, Brinell 148.
D—10 Minutes at 2000 degrees Fahr., quenched, Brinell 146.

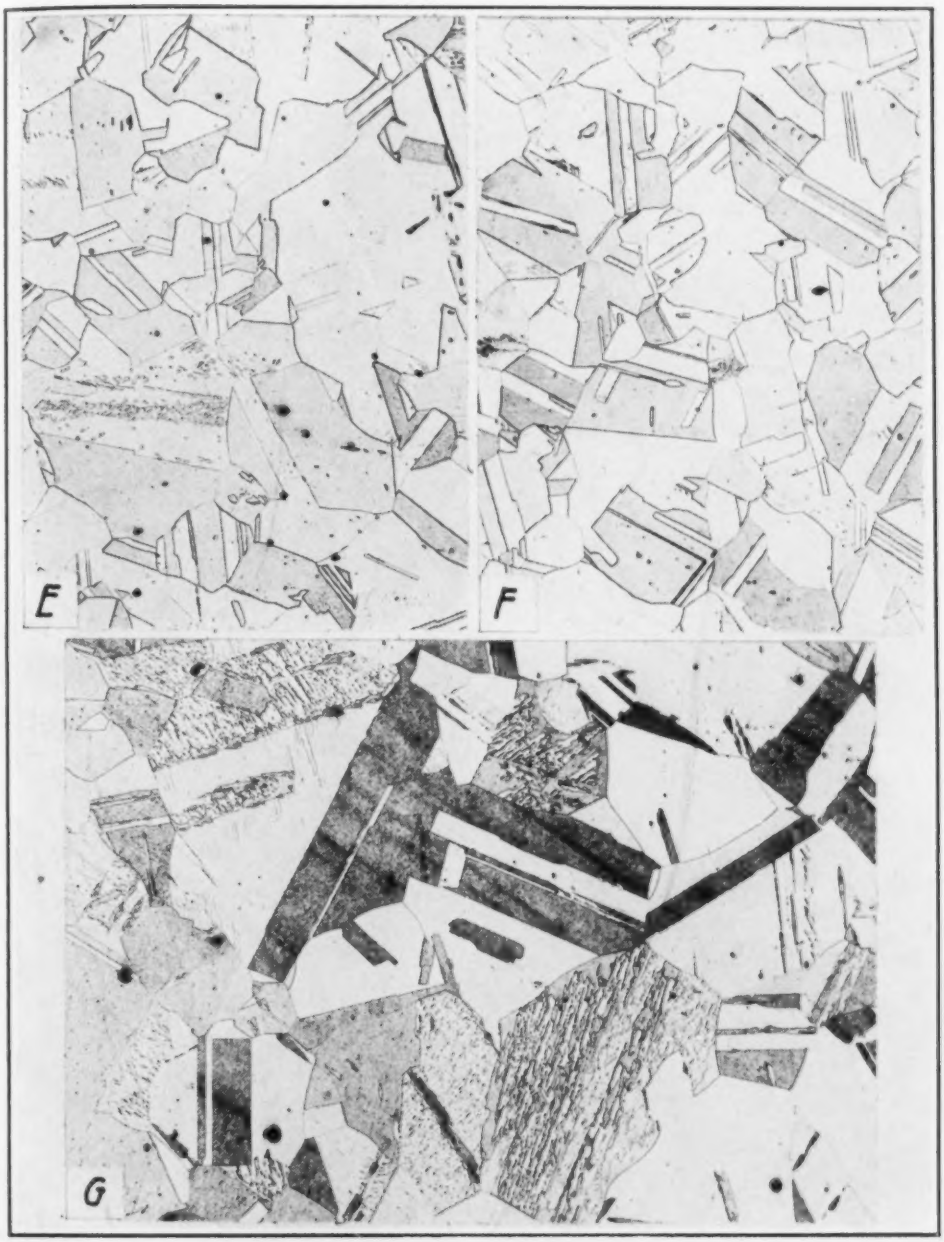


Fig. 1—Continued from Opposite Page.
E—3 Hours at 2000 degrees Fahr., quenched, Brinell 139.
F—10 Minutes at 2150 degrees Fahr., quenched, Brinell 143.
G—3 Hours at 2150 degrees Fahr., quenched, Brinell 134.

Physical properties representative of various grain sizes obtained from these treatments, are given in Table I. The foregoing experiments were purely of qualitative nature to indicate, in a general way, the influence of time and temperature of heat treatment on grain size

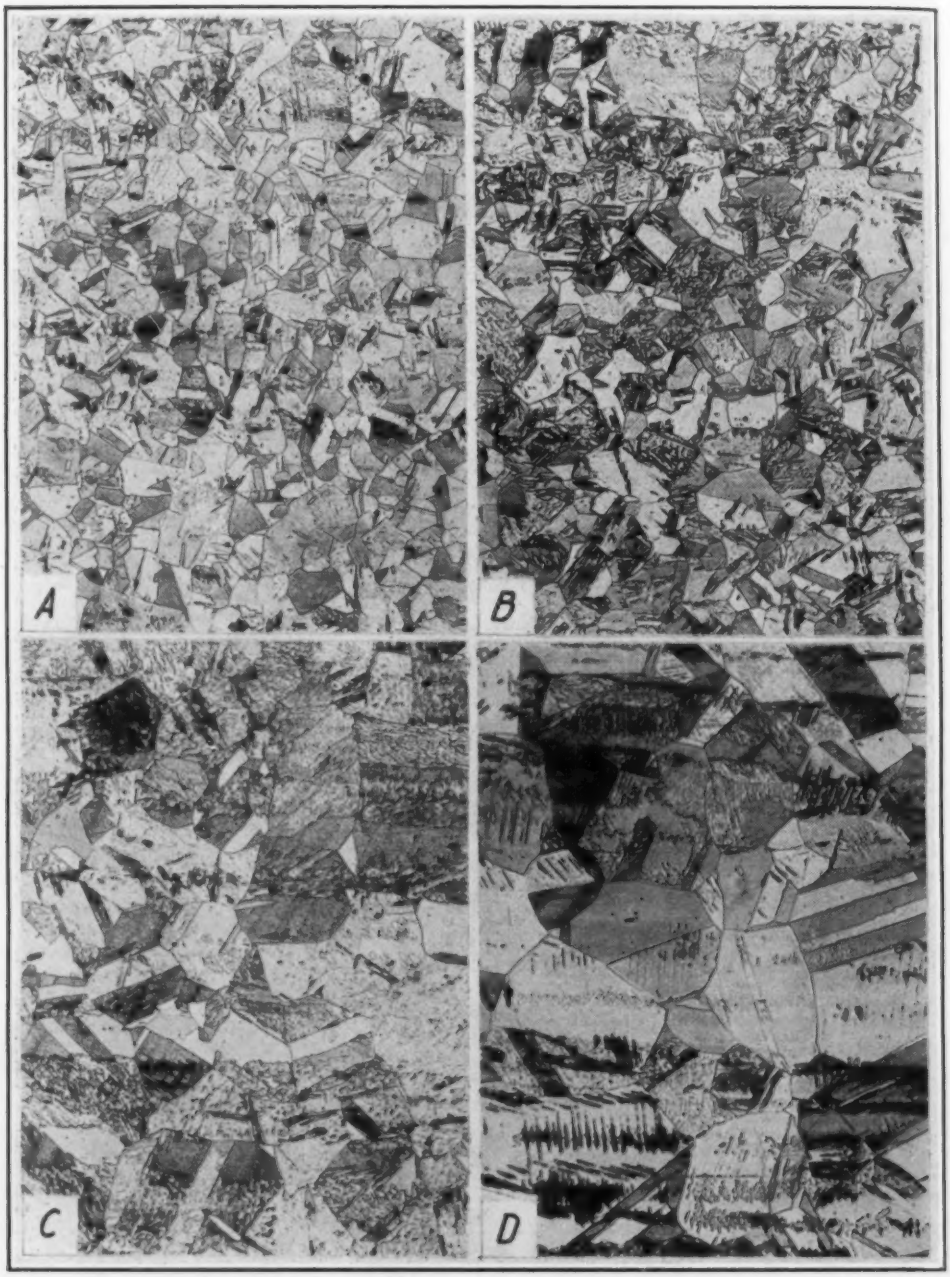


Fig. 2—Photomicrographs of Grain Size of 0.056 Per Cent Carbon, Hot-Rolled "18-8" alloy, Heat treated at Various Temperatures. Etched with "Chrome-regia." × 100.
A—45 Minutes at 1800 degrees Fahr., quenched.
B—45 Minutes at 1900 degrees Fahr., quenched.
C—45 Minutes at 2000 degrees Fahr., quenched.
D—45 Minutes at 2100 degrees Fahr., quenched.

of the 18-8 alloy. The influence of the degree of strain present prior to heating was not considered in connection with these tests. As is

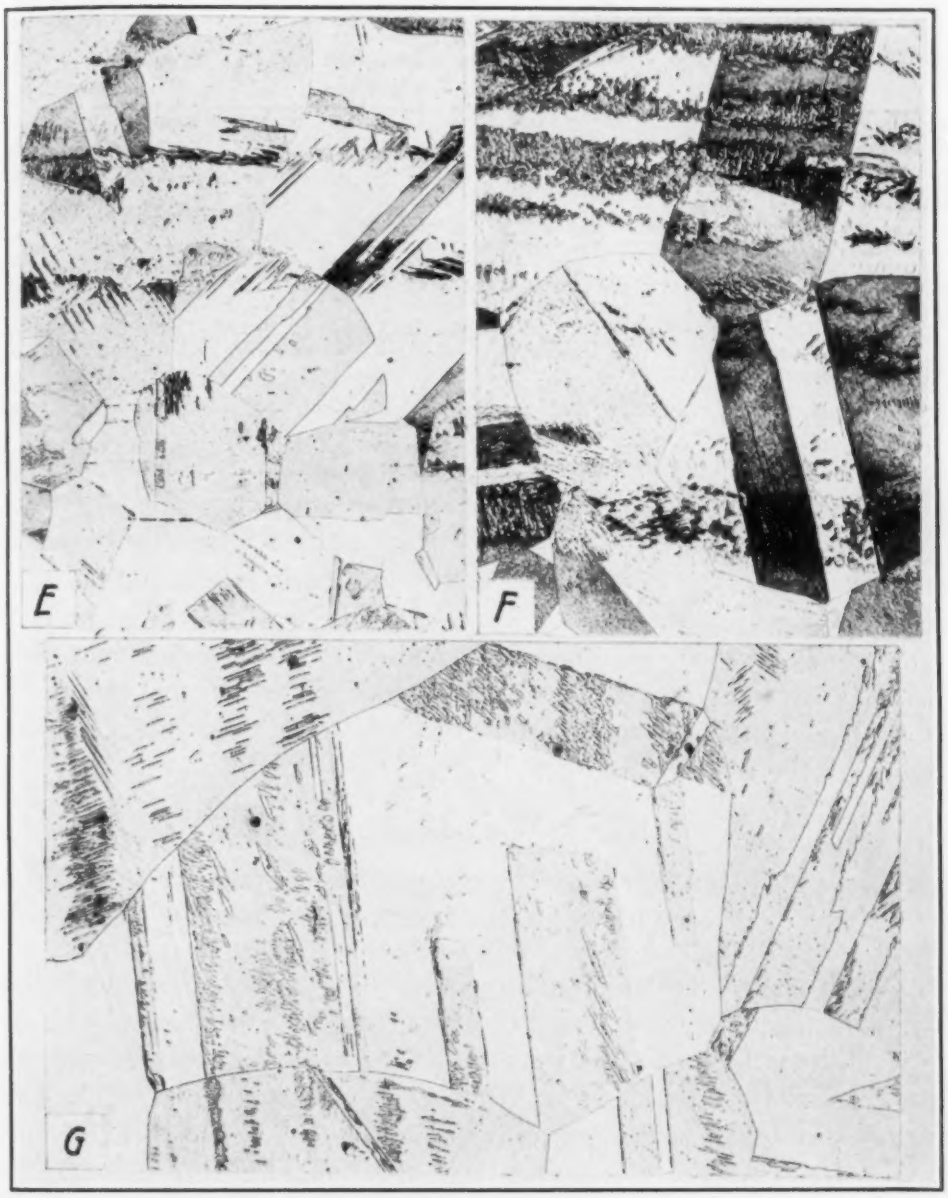


Fig. 2—Continued from Opposite Page.
E—45 Minutes at 2200 degrees Fahr., quenched.
F—45 Minutes at 2300 degrees Fahr., quenched.
G—45 Minutes at 2400 degrees Fahr., quenched.

Note: The structures shown are typical of low carbon "18-8" alloy. The banding present is likely due to primary or dendritic segregation leaving certain areas either carbon or nickel-poor. Rolled low carbon products exhibit such banded structures, which may be partially or wholly removed by diffusion on combined mechanical work and heat treatment. Cold work during preparation of the samples for microscopic examination may cause certain markings within the grains. The higher carbon or nickel content alloys are not similarly affected because of their greater stability, see Fig. 14.

well known, this factor affects recrystallization and grain growth.

Table I
Physical Properties of 0.056 Per Cent Carbon 18-8 Alloy as Affected by Heat Treating Temperature

Condition or Treatment	Ult. Strength Lbs./Sq. In.	Yield Pt. Lbs./Sq. In.	Elong. % in 2"	Red. of Area %	Brinell Hardness	Charpy* Ft. Lbs.
Hot-Rolled	106,700	46,575	51.5	71.4	170	83.5
1800° F., quench	102,075	36,575	54.25	73.5	156	85.0
1900° F., quench	102,275	37,025	60.25	73.15	149	79.5
2000° F., quench	101,225	33,975	55.0	71.4	143	91.0
2100° F., quench	100,887	33,600	55.25	71.4	137	81.0
2200° F., quench	99,412	33,500	57.0	70.7	137	96.0
2300° F., quench	94,625	31,475	58.7	71.4	137	101.5
2400° F., quench	95,825	30,000	58.2	71.3	131	101.5

Note: Average value of two tests, 0.505-inch diameter, 2-inch gage length specimens, heated ¾ hour of an hour at the temperatures indicated, quenched in water and tested at room temperature. *A.S.S.T. Charpy Specimens, drilled notch.

The term "heat treatment" used throughout this paper is nearly synonymous with the ordinary term anneal; however, in the austenitic steel alloys, this anneal may have the triple objects of: strain removal, preservation of the austenitic structure and carbide solution, so that it appears preferable to describe it as "heat treatment." Furthermore, the annealing of ordinary steels for grain refinement and ductility is accomplished by slowly cooling, while the austenitic chromium-nickel steel alloys are rapidly cooled and ductility increases with increase in grain size.

Part II

Effect of Grain Size on Physical Properties at Elevated Temperature and on Corrosion Resistance After Heating

This part of the investigation was undertaken to determine the effect of grain size, as induced by initial heat treatment, on the short time ultimate strength, the ductility at elevated temperature and on the corrosion resistance after heating at a temperature within the carbide precipitation range. A comparative study of 18-8 alloy of two carbon contents is made through the temperature range 800 to 1700 degrees Fahr. (425 to 925 degrees Cent.) inclusive, which temperatures are, respectively, below the carbide precipitation temperature on long heating and just below the temperature of appreciable carbide solubility.

Composition of Materials

The materials employed consisted of ⅞-inch diameter, hot-rolled 18-8 alloy rods of the following compositions:

	Per Cent	Per Cent
Carbon	0.054	0.14
Manganese	0.40	0.31
Sulphur	0.012	0.011
Phosphorus	0.020	0.008
Silicon	0.37	0.43
Chromium	18.30	17.41
Nickel	9.22	9.56

Heat Treatment of Specimens

A sufficient number of test specimens were cut from the 7/8-inch rods of each material, to give tensile specimens for short time high temperature tests through the range 800 to 1700 degrees Fahr. (425 to 925 degrees Cent.) by 100-degree Fahr. intervals, for both one hour and 150 hours at temperature, before pulling. A total of 160 test specimens were cut, of which 40 were left in the "hot-rolled" condition and 40 each were heat treated by heating one hour at 1900 degrees Fahr. (1040 degrees Cent.), 2100 degrees Fahr. (1150 degress Cent.) and 2300 degrees Fahr. (1260 degrees Cent.) respectively, and subsequently quenched in water. Procedure consisted of placing each group of specimens in a hot furnace, allowing them to remain at temperature one hour after the furnace had again reached the chosen temperature.

Temperatures of 1900 degrees Fahr. (1040 degrees Cent.), 2100 degrees Fahr. (1150 degrees Cent.) and 2300 degrees Fahr. (1260 degrees Cent.) were selected from the preliminary experiments on heating as having a sufficient difference between temperatures to cause a corresponding difference in the grain size of the alloy treated at these respective temperatures. The "hot-rolled" rod was used as representing the smallest grain size available.

Test Procedure

After heat treatment as previously described, one-half of the quantity of the 7/8-inch round 0.05 per cent and 0.14 per cent carbon specimens, were machined into 0.505-inch diameter 2-inch gage length, threaded end test pieces. Short time tensile tests were made using an electric resistance tube furnace supported in a 60,000 pound capacity, universal testing machine. A temperature controller was used for bringing up and holding the specimen at the desired temperature. (In view of the large amount of elevated temperature test work done in recent years, it does not appear necessary to describe the apparatus

used in detail, as the usual equipment for such tests is well known. The temperatures recorded in the data are approximate only and are correct to plus or minus 15 degrees Fahr. The difference in temperature between successive tests through the temperature range studied, was approximately 100 degrees Fahr. (38 degrees Cent.) which was considered more important than extremely accurate temperature values.)

After reaching temperature, all test pieces were maintained one hour at temperature before pulling to ensure thorough and even heating. This first group of 0.05 per cent and 0.14 per cent carbon alloy tests were pulled immediately after the heat treatments given with only the one hour heating period, and these have been designated in the data following as "short time tests, one hour at temperature."

The second half of the 7/8-inch diameter specimens were separately heated for 150 hours at the temperatures at which they were later pulled. This heating was for the purpose of partially establishing equilibrium in the alloy to obtain an indication as to the probable properties after long continued service. The time element was obviously too long to permit holding the individual test specimens in the furnace of the testing machine, consequently, the samples were treated in groups in separate furnaces equipped with controllers. Each group consisting of, hot-rolled, 1900 degrees Fahr. (1040 degrees Cent.), 2100 degrees Fahr. (1150 degrees Cent.) and 2300 degrees Fahr. (1260 degrees Cent.) quenched 0.05 and 0.14 per cent carbon test pieces, was held 150 hours at temperatures corresponding to the temperatures selected for study (for example, specimens to be pulled at 800 degrees Fahr. (425 degrees Cent.) were held 150 hours at 800 degrees Fahr. (425 degrees Cent.); those to be pulled at 900 degrees Fahr. (480 degrees Cent.) were held 150 hours at 900 degrees Fahr. (480 degrees Cent.) and so on.)

After the 150-hour heating period, all specimens were removed from the furnaces and allowed to cool in air to room temperature. Due to sluggishness of transformation, it is believed that cooling in such manner did not seriously change or interfere with the characteristics established in the 150-hour heating period. Similar 0.505-inch diameter 2-inch gage length, threaded end test specimens were then machined up and short time tensile tests made, after holding one hour at pulling temperature, as before. This group of tests, which were heated a considerable time before testing are designated as "short time tests, 150 hours at temperature."

All tests were made using the same testing machine, furnace, temperature controller and couple and employing, in every case, a cross-head speed on the testing machine of 0.08-inch per minute. The slowest pulling speed available was used as more nearly representing failure by creep, due to overheating, as occurs in practice. The time required for breaking the specimens from first application of load to rupture varied considerably and was dependent on the ductility of the individual specimen. This time varied from less than two minutes to 12 or 15 minutes in the most ductile specimens.

Physical Properties at Elevated Temperatures

The effects of heat treatment on physical properties at elevated temperature, after one hour and 150 hours heating, are shown in Tables II to V inclusive. These tables give the short time tensile strength and ductility, as measured by per cent elongation and per cent reduction of area, for hot-rolled and 1900 degrees Fahr. (1040 degrees Cent.), 2100 degrees Fahr. (1150 degrees Cent.) and 2300 degrees Fahr. (1260 degrees Cent.) quenched 0.05 per cent and 0.14 per cent carbon, 18-8 alloy. For convenience of comparison, the results are plotted and shown in Figs. 3 to 10. There are also appended Plates 1 to 16 inclusive, which are photographs of the fractured test specimens grouped by material and treatment. (Pages 717-732.)

Discussion of Results of Short Time Tests

a. 0.05 per cent carbon, 18-8 alloy

Comparison of the test results on the 0.05 per cent carbon material shows conclusively that the condition of the alloy, as induced by heat treatment, governs to a great extent, the ductility on rupture and affects to a certain degree, the short time strength at elevated temperature. At temperatures from 800 to 1200 degrees Fahr. (425 to 650 degrees Cent.) inclusive, on one hour tests, the strength is lower, the higher the temperatures from which the alloy was originally quenched, and in the main this is true all through the test range. An exception appears, see Fig. 3, in the 2300 degrees Fahr. (1260 degrees Cent.) quenched alloy, tested at 1600 degrees Fahr. (870 degrees Cent.).

In the 150-hour tests, the hot-rolled and 1900 degrees Fahr. (1040 degrees Cent.) quenched alloys show somewhat greater

Table II

Effect of Heat Treatment on Physical Properties of 0.05 Per Cent Carbon, 18-8 Alloy, at Elevated Temperatures, Short Time Test, One Hour at Temperature

Temp. of Test Deg. Fahr.	Hot-Rolled	1900 Deg. Fahr. Quenched	2100 Deg. Fahr. Quenched	2300 Deg. Fahr. Quenched
		Ultimate Strength		
800	60,710	58,440	56,690	.....
900	58,310	55,345	54,252	51,848
1000	54,245	51,330	50,700	48,800
1100	47,902	46,303	44,705	41,600
1200	38,261	37,512	35,314	35,589
1300	30,819	28,821	29,040	25,750
1400	32,750	29,100	28,750	21,050
1500	18,530	17,882	15,580	15,934
1600	13,650	11,900	9,220	14,700
1700	9,950	9,323	8,542	7,592
		Reduction of Area in Per Cent		
800	69.3	70.6	71.4	....
900	71.1	72.3	71.4	68.2
1000	67.5	66.5	70.6	65.4
1100	57.5	51.7	50.6	39.4
1200	58.8	50.6	30.8	31.2
1300	61.1	51.1	28.9	13.0
1400	71.0	54.0	24.8	10.4
1500	42.8	31.2	15.9	5.0
1600	38.8	30.5	11.9	5.9
1700	35.0	40.8	25.8	5.8
		Per Cent Elongation in 2 Inches		
800	45.5	46.0	46.5	....
900	45.0	46.0	46.0	47.0
1000	43.5	44.0	44.5	45.0
1100	42.5	40.0	39.0	34.0
1200	57.0	49.0	31.0	26.0
1300	60.5	56.0	27.0	14.0
1400	49.0	49.0	17.5	8.5
1500	49.5	40.0	16.0	8.5
1600	43.5	37.5	14.5	6.5
1700	48.0	52.5	38.0	7.0

strength from 800 to 1000 degrees Fahr. (425 to 540 degrees Cent.) inclusive. Consult Fig. 4. Above 1000 degrees Fahr. (540 degrees Cent.) the strengths are more nearly uniform, although the hot-rolled condition exhibits slightly greater values than the quenched conditions up to 1500 degrees Fahr. (815 degrees Cent.).

The ductility of the alloy, after one hour heating, is unaffected by heat treatment until a temperature of 1000 degrees Fahr. (540 degrees Cent.) has been passed. At 1100 degrees Fahr. (595 degrees Cent.) both reduction of area and elongation diminish as the initial heat treating temperature, to which the specimens were subjected, increases. It will be observed that the hot-rolled and to a lesser extent the 1900 degrees Fahr. (1040 degrees Cent.) quenched alloy maintains ductility up to 1400 degrees Fahr. (760 degrees Cent.) while the alloy quenched from higher temperatures shows a rapid decrease in this property.

Table III

Effect of Heat Treatment on Physical Properties of 0.05 Per Cent Carbon, 18-8 Alloy, at Elevated Temperatures. Short Time Test, 150 Hours at Temperature

Temp. of Test Deg. Fahr.	Hot-Rolled	1900 Deg. Fahr. Quenched	2100 Deg. Fahr. Quenched	2300 Deg. Fahr. Quenched
		Ultimate Strength		
800	62,680	57,940	56,690	54,030
900	59,563	57,143	53,999	51,948
1000	54,145	53,144	49,924	49,472
1100	47,172	47,870	48,052	45,763
1200	38,586	36,716	36,313	35,232
1300	36,986	35,714	36,090	36,391
1400	27,700	25,100	23,500	23,550
1500	15,288	7,528	9,090	5,965
1600	14,300	15,500	15,100	14,650
1700	6,543	6,089	4,812	5,363
		Reduction of Area in Per Cent		
800	69.7	69.7	71.8	64.8
900	64.0	71.3	71.3	73.5
1000	66.8	71.5	64.1	61.3
1100	68.6	65.8	59.6	46.9
1200	70.8	65.8	41.0	34.2
1300	71.4	57.3	44.0	34.2
1400	63.5	50.6	27.7	26.5
1500	42.6	43.7	29.2	15.6
1600	47.7	45.8	37.9	24.1
1700	45.8	55.8	61.0	13.8
		Per Cent Elongation in 2 Inches		
800	46.0	46.5	46.5	46.0
900	40.0	44.0	47.0	47.0
1000	44.0	50.0	40.0	45.0
1100	48.0	43.0	46.0	38.5
1200	57.0	50.0	39.0	34.0
1300	51.0	51.0	33.0	32.0
1400	56.0	40.0	25.0	19.0
1500	49.0	45.5	21.5	12.0
1600	53.0	52.5	33.0	17.5
1700	60.5	58.0	59.0	22.0

The temperature of minimum ductility, on one hour's heating, varies somewhat depending on heat treatment received, being roughly as follows:

Hot-rolled, 1700 degrees Fahr. (925 degrees Cent.).

1900 degrees Fahr., quenched, 1600 degrees Fahr. (870 degrees Cent.).

2100 degrees Fahr., quenched, 1600 degrees Fahr. (870 degrees Cent.).

2300 degrees Fahr., quenched, 1500 degrees Fahr. (815 degrees Cent.).

In the 2300 degrees Fahr. (1260 degrees Cent.), quenched alloy, there is little difference in either elongation or reduction of area through the range 1400 degrees Fahr. (760 degrees Cent.) to 1700 degrees Fahr. (760 to 925 degrees Cent.). This is partially true, also, of the alloy quenched from 2100 degrees Fahr. (1150 degrees

Table IV

Effect of Heat Treatment on Physical Properties of 0.14 Per Cent Carbon, 18-8 Alloy at Elevated Temperature, Short Time Test One Hour at Temperature

Temp. of Test Deg. Fahr.	Hot-Rolled	1900 Deg. Fahr. Quenched	2100 Deg. Fahr. Quenched	2300 Deg. Fahr. Quenched
		Ultimate Strength		
800	74,000	73,200	70,000	69,200
900	72,000	71,000	65,800	68,700
1000	67,200	68,450	61,200	64,700
1100	63,900	62,300	52,000	57,800
1200	55,300	51,900	44,100	46,800
1300	40,100	44,300	34,300	40,500
1400	30,900	32,050	26,950	29,250
1500	24,250	23,100	21,350	23,050
1600	16,190	16,060	15,130	9,250
1700	14,740	12,450	14,400	12,750
		Reduction of Area in Per Cent		
800	71.3	74.5	70.8	71.1
900	57.7	73.0	64.7	67.4
1000	68.3	72.2	46.3	61.5
1100	56.6	49.5	35.5	36.3
1200	56.1	34.5	25.2	23.9
1300	38.0	31.3	22.3	17.1
1400	64.6	44.7	30.2	19.9
1500	41.1	29.7	22.8	13.8
1600	36.1	33.9	27.6	25.4
1700	44.5	38.7	31.6	26.1
		Per Cent Elongation in 2 Inches		
800	53.0	62.0	45.5	56.0
900	49.0	56.0	46.5	49.5
1000	49.5	51.5	35.5	46.0
1100	38.5	39.5	28.5	33.5
1200	40.0	30.0	18.0	23.0
1300	26.5	26.5	22.0	15.0
1400	57.5	45.0	31.0	21.0
1500	45.0	23.5	21.5	14.0
1600	37.0	37 0	28.0	28.0
1700	56.0	35.5	26.0	28.5

Cent.); however, improvement is shown at 1700 degrees Fahr. (925 degrees Cent.).

Fig. 5 shows uniform ductility regardless of treatment in both elongation and reduction of area to 1000 degrees Fahr. (540 degrees Cent.). At 1100 degrees Fahr. (595 degrees Cent.), which temperature is sufficient for carbide precipitation, even on a heating period as short as one hour, the ductility is affected in a degree which is dependent on the grain size as induced by the initial heat treatment. The hot-rolled, and to a lesser extent the 1900 degrees Fahr. (1040 degrees Cent.) quenched alloy starts improving in ductility which rises to a maximum reduction of area at 1400 degrees Fahr. (760 degrees Cent.) with maximum elongation at 1300 degrees Fahr. (705 degrees Cent.). On the other hand, the specimens quenched from higher temperatures and representing large-grained alloy, diminish rapidly in ductility as the temperature increases from 1100 degrees Fahr. (595 degrees Cent.).

Table V

Effect of Heat Treatment on Physical Properties of 0.14 Per Cent Carbon, 18-8 Alloy at Elevated Temperature, Short Time Test, 150 Hours at Temperature

Temp. of Test Deg. Fahr.	Hot-Rolled	1900 Deg. Fahr. Quenched	2100 Deg. Fahr. Quenched	2300 Deg. Fahr. Quenched
		Ultimate Strength		
800	74,700	73,200	71,800	69,100
900	70,390	69,520	69,250	67,810
1000	69,320	70,025	67,280	64,850
1100	64,200	66,170	63,100	59,250
1200	50,800	54,650	51,360	46,845
1300	41,100	46,350	46,550	42,850
1400	14,650	21,370	26,170	31,000
1500	21,675	24,375	20,750	23,400
1600	17,050	17,080	17,900	16,800
1700	16,133	16,336	14,785	15,280
		Reduction of Area in Per Cent		
800	62.6	64.8	57.8	55.6
900	66.6	70.7	70.4	69.0
1000	64.6	65.8	59.9	51.7
1100	58.1	56.9	44.0	31.9
1200	56.2	35.4	31.6	25.5
1300	62.3	36.7	30.8	38.8
1400	46.6	58.8	45.3	41.9
1500	48.6	36.3	15.3	22.3
1600	38.5	35.3	31.2	30.0
1700	42.8	39.1	36.3	33.4
		Per Cent Elongation in 2 Inches		
800	49.0	51.5	48.0	48.0
900	47.0	50.0	51.0	55.0
1000	43.5	47.5	45.0	45.0
1100	38.0	45.0	37.5	30.0
1200	41.0	31.0	26.0	20.0
1300	49.0	35.0	24.0	17.5
1400	51.0	65.0	51.0	36.0
1500	53.5	31.5	14.0	20.0
1600	38.5	42.0	32.5	26.0
1700	32.0	35.0	42.0	36.0

On heating 150 hours before testing, Fig. 6, the same general characteristics are found as in the case of the one hour heating. The fine-grained material has much better ductility than the coarse-grained, above 1000 degrees Fahr. (540 degrees Cent.). The hot-rolled alloy shows the greatest ductility which it maintains to 1300 degrees Fahr. (705 degrees Cent.), having at that temperature 71.4 per cent reduction of area and 51.0 per cent elongation in 2 inches.

It is interesting to note, on comparison of the elongation and reduction figures given in Table II and III, that improvement occurs on heating 150 hours as against heating one hour. This is particularly noticeable in the 2100 and 2300 degrees Fahr. (1150 and 1260 degrees Cent.) quenched alloy, and is probably due to reparation by diffusion of the material in the vicinity of grain boundaries, which has been altered by carbide precipitation. Long heating, because of the time necessary for diffusion at these temperatures, causes improve-

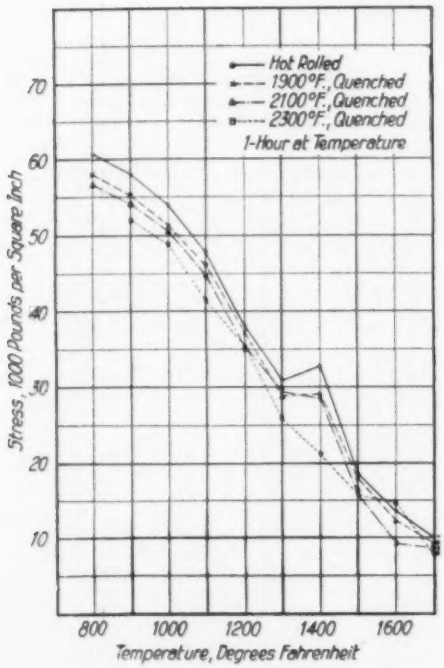


Fig. 3—Effect of Heat Treatment on the Short-Time Ultimate Strength of 0.05 Per Cent Carbon, "18-8" Alloy, on 1 Hour Heating.

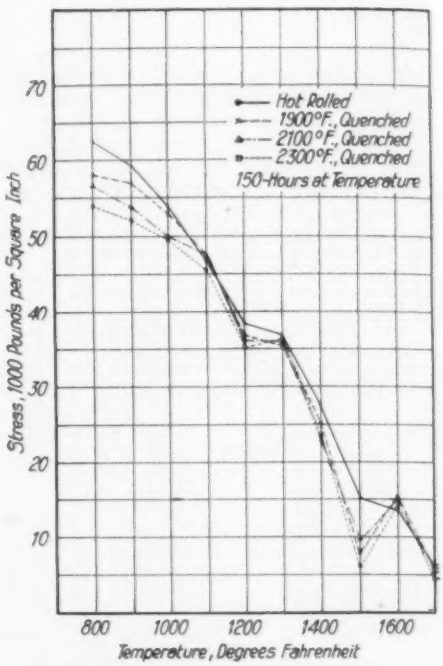


Fig. 4—Effect of Heat Treatment on the Short-Time Ultimate Strength of 0.05 Per Cent Carbon, "18-8" Alloy, on 150 Hours Heating.

ment in ductile properties over that found on short heating. The temperature of minimum ductility on 150 hours heating is 1500 degrees Fahr. (815 degrees Cent.) for all conditions of heat treatment.

Again considering the strength values given in Fig. 3, it will be seen that strength is maintained between 1300 and 1400 degrees Fahr. (705 and 760 degrees Cent.) in spite of the 100 degrees Fahr. (38 degrees Cent.) rise in temperature. This is true for all conditions except the 2300 degrees Fahr. quenched state. The hot-rolled alloy even increases slightly in strength. On 150 hours heating, this same phenomenon occurs, but due to the time effect in establishing equilibrium, it now occurs between 1200 and 1300 degrees Fahr. (650 and 705 degrees Cent.). An inferred explanation of this maintenance in strength, is that it corresponds to the Ac_1 transformation point occurring in the various carbon and low alloy steels and represents the temperatures at which some alpha iron is formed. According to Lester[6], this may be described as due to stiffening of the austenite grains, from precipitation of alpha iron, which causes inter-

[6]H. H. Lester, "The Brittle Range in 18 and 8 Chromium-Nickel-Iron." TRANSACTIONS, American Society for Steel Treating, Vol. 16, November, 1929, p. 743.

ference to slip. The alpha iron may be formed by mechanical work due to deformation during pulling of the specimens. (Alpha iron may be formed also by heating 0.05 per cent carbon, 18-8 alloy at

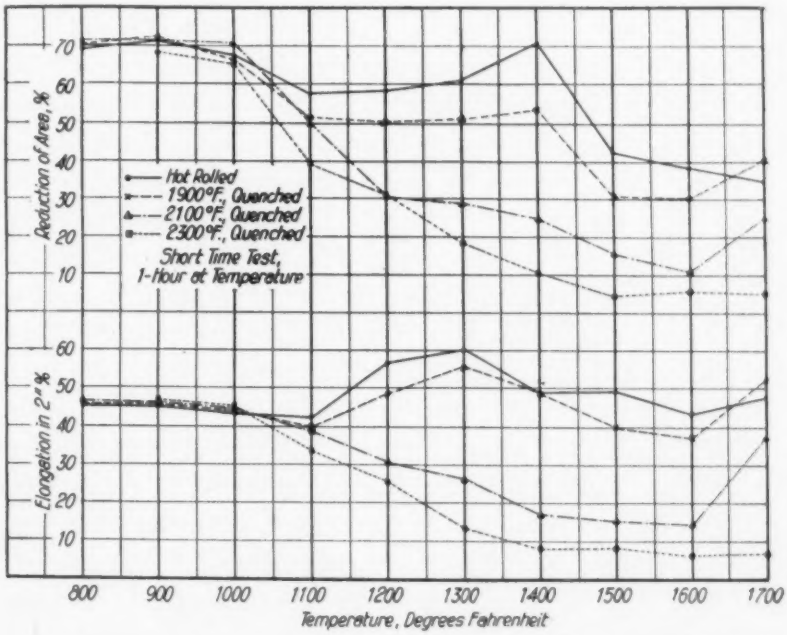


Fig. 5—Effect of Heat Treatment on the Ductility of 0.05 Per Cent Carbon, "18-8" Alloy at Elevated Temperatures. Short Time Test, 1 Hour at Temperature.

certain elevated temperatures without deformation). (Note by the author.)

Further study of Fig. 4 shows the strength to drop uniformly between 1300 and 1500 degrees Fahr. (705 and 815 degrees Cent.). At 1600 degrees Fahr. (870 degrees Cent.) an appreciable increase in strength occurs, excepting for the hot-rolled alloy. This increase in strength might be attributed to the Ac_3 transformation where the alpha iron formed at the lower temperatures is again converted to gamma iron. Ordinary steels and even pure iron[7] show an increase in short time strength at temperatures corresponding to their Ac_3 transformation points, which is the temperature at which complete change to gamma iron or austenite occurs. Austenite being superior in strength to alpha iron causes an increase in the strength because the alloy has fully returned to the austenitic condition at this temperature.

[7]Albert Sauveur, "Steel at High Temperatures," TRANSACTIONS, American Society for Steel Treating, Vol. 17, March, 1930, p. 410.

b. 0.14 Per Cent Carbon, 18-8 Alloy

In general, the 0.14 per cent carbon alloy shows somewhat greater short time strength than the 0.05 per cent carbon alloy, the difference being about 13,000 pounds per square inch at 800 degrees

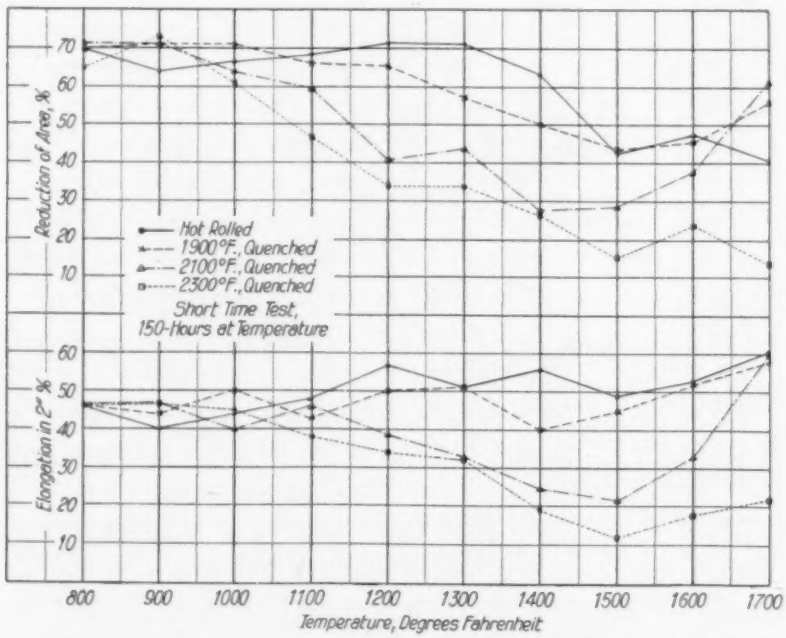


Fig. 6—Effect of Heat Treatment on the Ductility of 0.05 Per Cent Carbon, "18-8" Alloy at Elevated Temperatures. Short Time Test, 150 Hours at Temperature.

Fahr. (425 degrees Cent.) and 5000 pounds per square inch at 1700 degrees Fahr. (925 degrees Cent.). This difference in strength is attributed to the greater amount of carbon contained in 0.14 per cent carbon material.

The one hour tests, Fig. 7, show smooth curves except for the 2300 degrees Fahr. (1260 degrees Cent.) quenched alloy at 1600 degrees Fahr. (870 degrees Cent.) where the strength drops considerably below the value for the same treatment at 1700 degrees Fahr. (925 degrees Cent.). This suggests again the Ac_3 transformation point. In the tests held 150 hours before pulling, Fig. 8, there is a suggestion of the Ac_1 point between 1200 and 1300 degrees Fahr. (650 to 705 degrees Cent.) indicated by change in slope of curves. The Ac_3 point is indicated at 1500 degrees Fahr. (815 degrees Cent.) particularly by the increase in strength of the hot-rolled and 1900 degrees Fahr. (1040 degrees Cent.) quenched alloy. These trans-

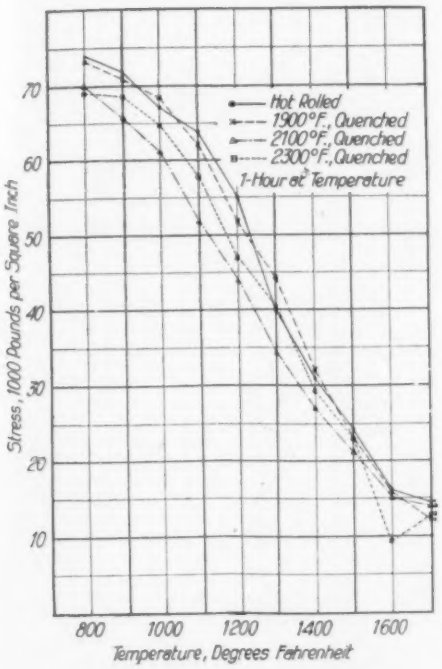


Fig. 7—Effect of Heat Treatment on the Short-Time Ultimate Strength of 0.14 Per Cent Carbon, "18-8" Alloy, on 1 Hour Heating.

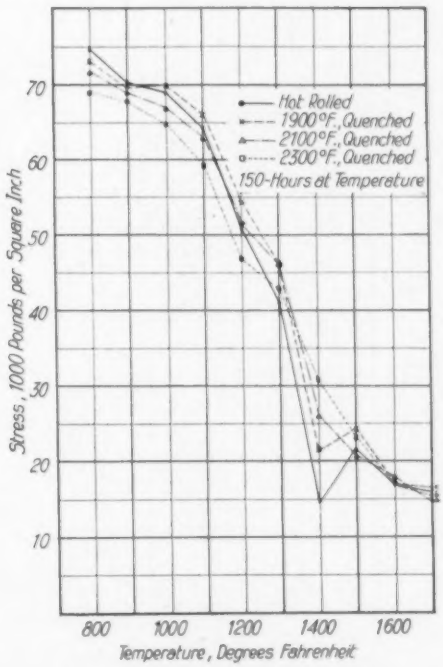


Fig. 8—Effect of Heat Treatment on the Short-Time Ultimate Strength of 0.14 Per Cent Carbon, "18-8" Alloy, on 150 Hours Heating.

formation points are not nearly as pronounced in the 0.14 per cent carbon alloy as in the 0.05 per cent carbon alloy, due to the greater stability of the austenite phase induced by the additional carbon present. At 1400 degrees Fahr. (760 degrees Cent.) there is considerable difference in strength, the coarse-grained being superior to the fine-grained alloys.

The ductility of the 0.14 per cent carbon alloy is affected by heat treatment in much the same manner as was the 0.05 per cent carbon alloy at elevated temperatures. Below 1000 degrees Fahr. (540 degrees Cent.) there is no great difference, but above this temperature, the trend of reduced ductility is evidenced both on the one hour and the 150 hour tests, Figs. 9 and 10. The fine-grained conditions show superiority over the coarse-grained conditions. Contrary to the 0.05 per cent carbon alloy, the higher carbon material shows minimum ductility at 1300 degrees Fahr. (705 degrees Cent.). There is also a low point at approximately 1500 degrees Fahr. (815 degrees Cent.) with an increase in ductility for all grain sizes on heating for one hour at 1400 degrees Fahr. (760 degrees Cent.).

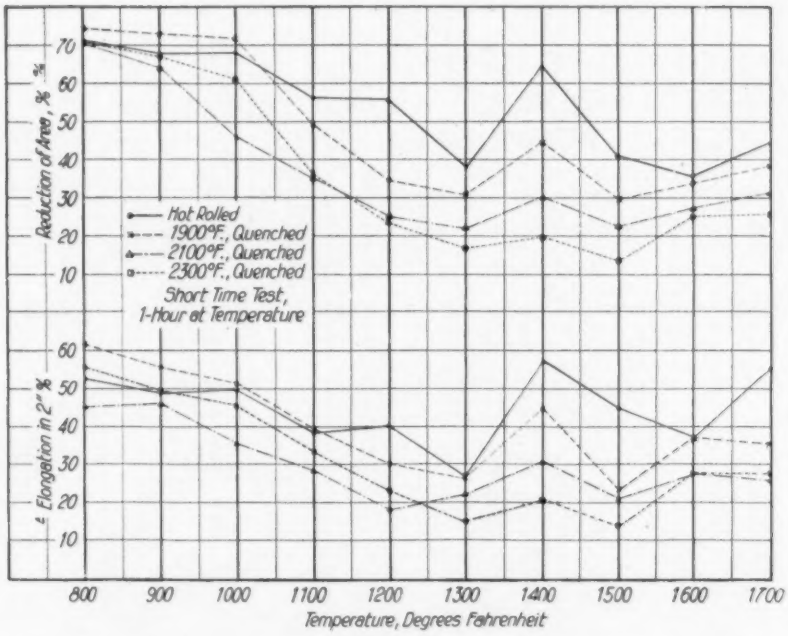


Fig. 9—Effect of Heat Treatment on the Ductility of 0.14 Per Cent Carbon, "18-8" Alloy at Elevated Temperatures. Short Time Test, 1 Hour at Temperature.

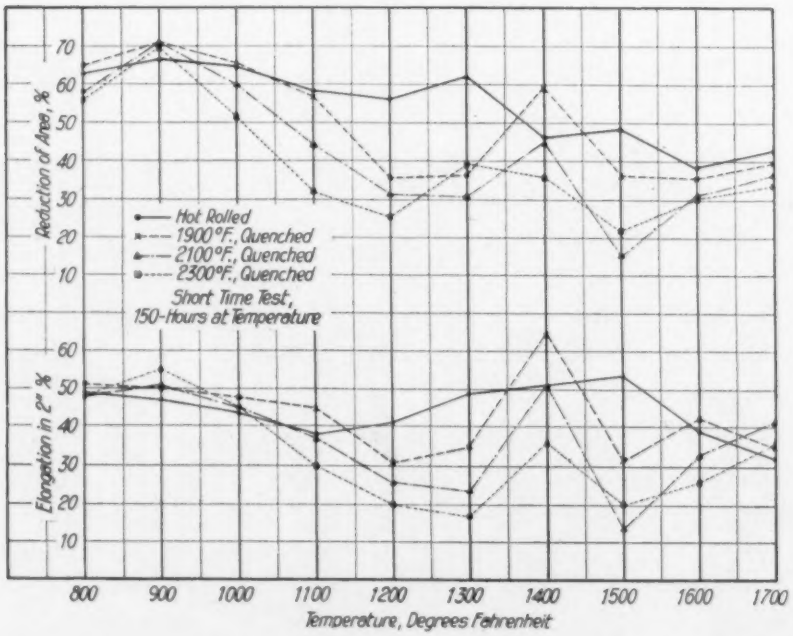


Fig. 10—Effect of Heat Treatment on the Ductility of 0.14 Per Cent Carbon, "18-8" Alloy at Elevated Temperatures. Short Time Test, 150 Hours at Temperature.

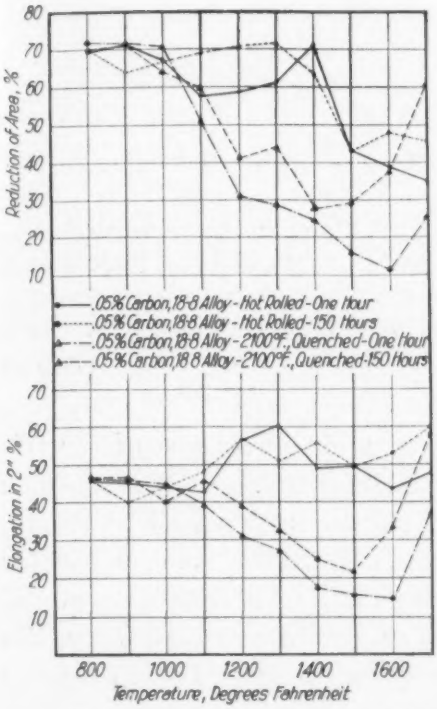

Reduction of Area, %
Elongation in 2" %
.05% Carbon, 18-8 Alloy - Hot Rolled - One Hour
.05% Carbon, 18-8 Alloy - Hot Rolled - 150 Hours
.05% Carbon, 18-8 Alloy - 2100°F., Quenched - One Hour
.05% Carbon, 18-8 Alloy - 2100°F., Quenched - 150 Hours
800 1000 1200 1400 1600
Temperature, Degrees Fahrenheit

Fig. 11—Comparison of the Ductility at Elevated Temperature of Hot-Rolled versus 2100-Degree Fahr. Quench of 0.05 Per Cent Carbon, "18-8" Alloy After 1 Hour and 150 Hours Heating.

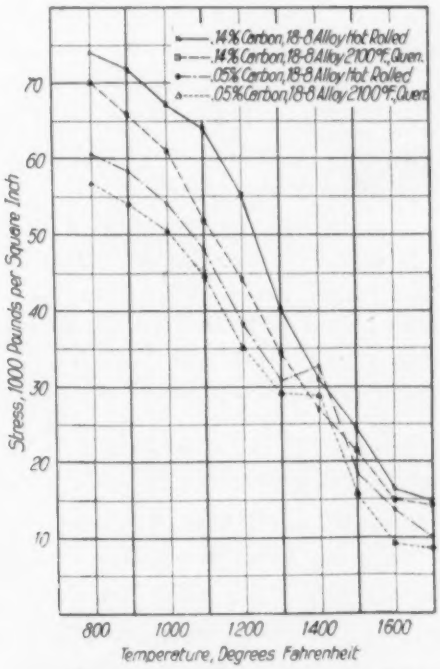

.14% Carbon, 18-8 Alloy Hot Rolled
.14% Carbon, 18-8 Alloy 2100°F. Quen.
.05% Carbon, 18-8 Alloy Hot Rolled
.05% Carbon, 18-8 Alloy 2100°F. Quen.
Stress, 1000 Pounds per Square Inch
800 1000 1200 1400 1600
Temperature, Degrees Fahrenheit

Fig. 12—Comparison of the Short-Time Ultimate Strength of 0.05 Per Cent Carbon, "18-8" Alloy and 0.14 Per Cent Carbon, "18-8" Alloy at Elevated Temperatures in the Hot-Rolled and 2100-Degree Fahr. Quenched Conditions. 1 Hour Tests.

Creep as Affected by Grain Size

The preceding discussion was given mainly to point out the characteristics of the alloy as disclosed by the elevated temperature tests, particularly with reference to ductility as affected by grain size. It has been shown by other investigators that the creep strength of, or the ability of the 18-8 alloy to carry constant load at high temperatures, may be affected by grain size. French, Kahlbaum and Peterson,[8] state:

"In the case of the wrought alloy containing about 0.15 per cent carbon, 18 per cent chromium and 8 per cent nickel, fine-grained and coarse-grained samples showed about equal load carrying ability at 990 degrees Fahr. (530 degrees Cent.), but the fine-grained were weaker than the coarse-grained at 1180 degrees Fahr. (640 degrees Cent.). This should not be taken as a recommendation of coarse-grained metals for high temperature service since frac-

[8]H. J. French, William Kahlbaum and A. A. Peterson, "Flow Characteristics of Special Fe-Ni-Cr Alloys and Some Steels at Elevated Temperatures," Bureau of Standards, *Journal of Research*, Vol. 5, No. 1, July, 1930, p. 182.

ture may occur with less total elongation than in the corresponding fine-grained metals and so counteract any advantages from lower rates of flow. There is also the possible added disadvantage of weakness in resisting shock."

Further, Kanter and Spring[9] in a recent publication draw the following conclusions regarding creep of the austenitic chromium-nickel steel (18-8 alloy).

"Austenitic chromium-nickel steel (18-8 alloy) when water-quenched from 2100 degrees Fahr. (1150 degrees Cent.) and therefore of large grain size is more resistant to flow than it is in the unaltered rolled condition, as shown at 1200, 1400 and 1600 degrees Fahr. (650, 760 and 870 degrees Cent.). It is apparent that treatments which produce increased grain size reduce creep in metals above the equi-cohesive temperature."

The material investigated by Kanter and Spring was of the following composition: carbon, 0.04 per cent; manganese, 0.50 per cent; silicon, 0.70 per cent; chromium, 19.02 per cent; nickel, 9.74 per cent.

While there will undoubtedly be some difference reflected in the ductility of 18-8 alloy under long time failure by creep at elevated temperatures, as against the short time results reported here, the somewhat greater advantage for creep in coarse-grained metal is more than offset by its poorer ductility on fracture, as compared with fine-grained metal. Comparison of the ductility of 0.05 per cent carbon, 18-8 in the hot-rolled and 2100 degrees Fahr. (1150 degrees Cent.) quenched conditions, on both one and 150 hours heating, is as shown in the curves contained in Fig. 11. Fig. 12 shows the comparative short time strength of 0.05 per cent and 0.14 per cent carbon, 18-8 alloy in the hot-rolled and 2100 degrees Fahr. (1150 degrees Cent.) quenched conditions, on the one hour heating period.

Microstructure

a. Grain Size

The grain size of the 0.05 and 0.14 per cent carbon alloys in the hot-rolled condition, and after heat treatment, consisting of heating one hour at 1900, 2100 and 2300 degrees Fahr. (1040, 1150 and 1260 degrees Cent.) respectively, followed by quenching in water is as shown in Figs. 13 and 14. The structures shown are average fields and are representative of the grain sizes contained in the specimens of each alloy tested at elevated temperatures.

[9] J. J. Kanter and L. W. Spring, "Some Long Time Tension Tests of Steel at Elevated Temperatures," *Proceedings*, American Society for Testing Materials, Vol. 30, Part I, 1930, p. 110.

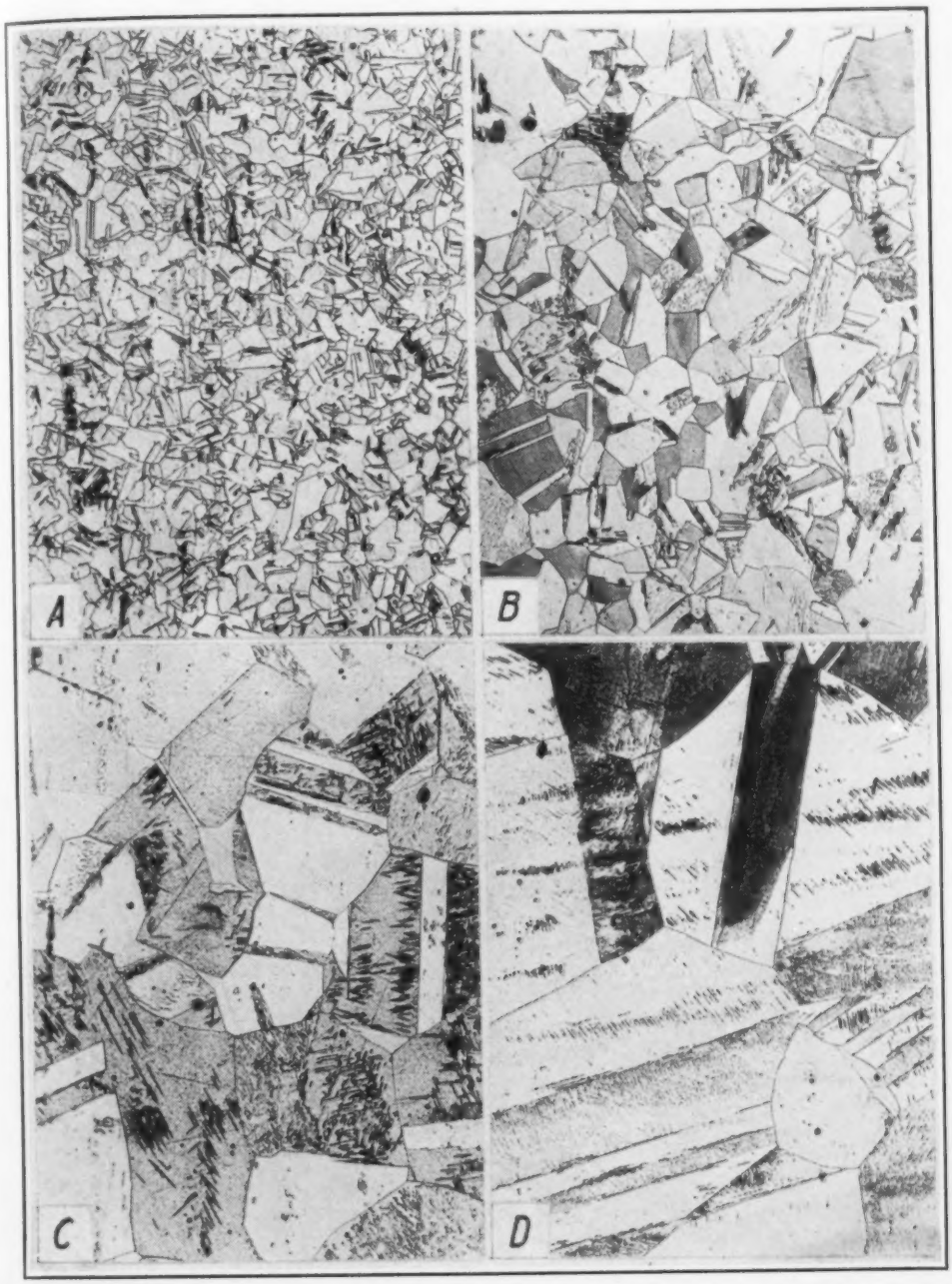


Fig. 13—Photomicrographs of Grain Size of 0.05 Per Cent Carbon "18-8" Alloy. All Specimens Etched with "Chrome-regia." × 100. A—"Hot-Rolled," Brinell 143. B—1900-Degree Fahr., (1040 Degrees Cent.) Quench, Brinell 137. C—2100-Degree Fahr. (1150 Degrees Cent.) Quench, Brinell 131. D—2300-Degree Fahr. (1260 Degrees Cent.) Quench, Brinell 131.

b. Grain Size After Heating

It would be difficult, because of the work involved, to present

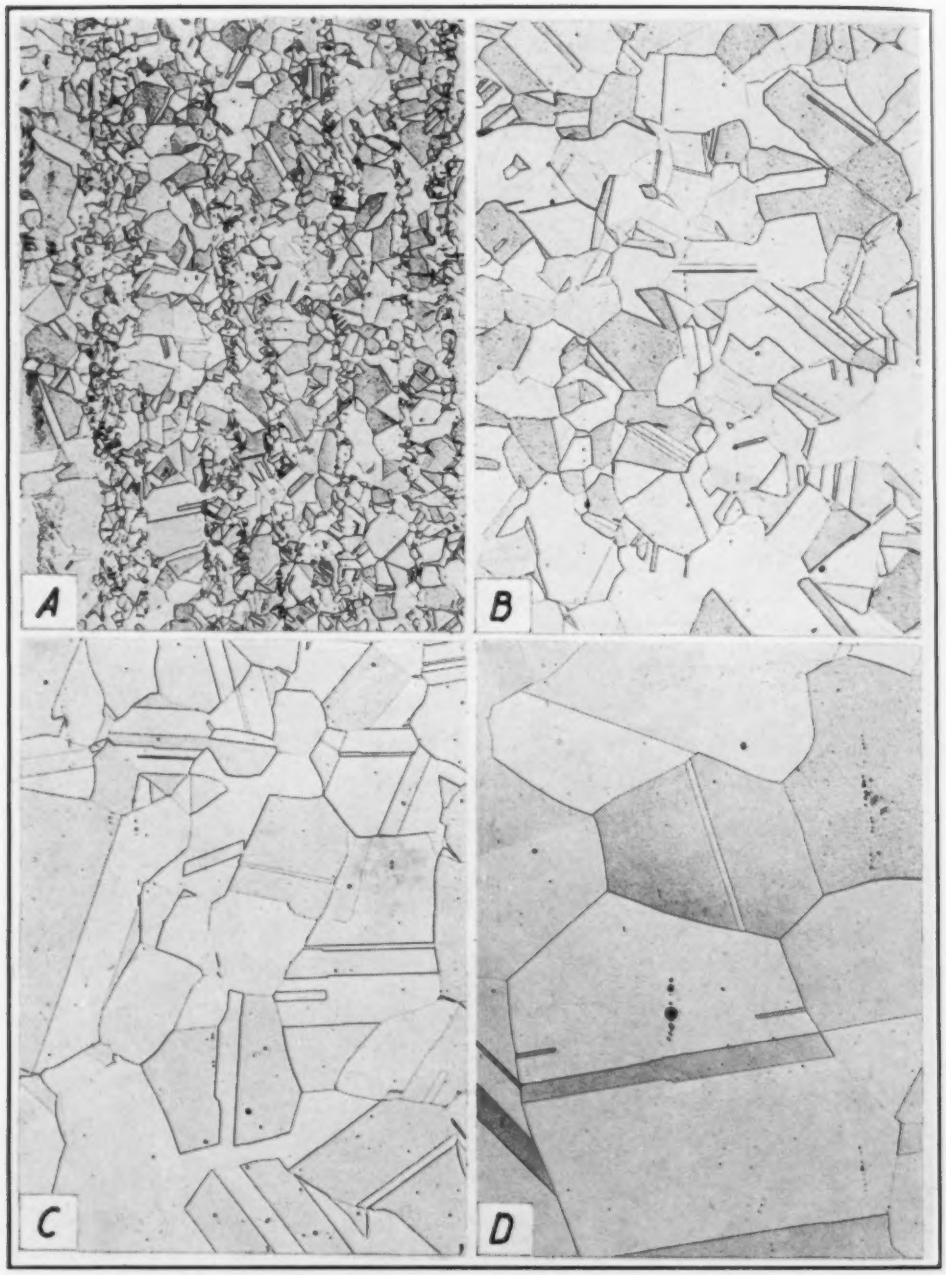


Fig. 14—Photomicrographs of Grain Size of 0.14 Per Cent Carbon, "18-8" Alloy. All Specimens Etched with "Chrome-regia." × 100. A—"Hot-Rolled," Brinell 159. B—1900-Degree Fahr. (1040 Degrees Cent.) Quench, Brinell 143. C—2100-Degree Fahr. (1150 Degrees Cent.) Quench, Brinell 131. D—2300-Degree Fahr. (1260 Degrees Cent.) Quench, Brinell 126.

photomicrographs of the structures of the 0.05 and 0.14 per cent carbon 18-8 alloy in the hot-rolled and heat treated conditions after 150 hours heating at temperatures through the range 800 to 1700 degrees

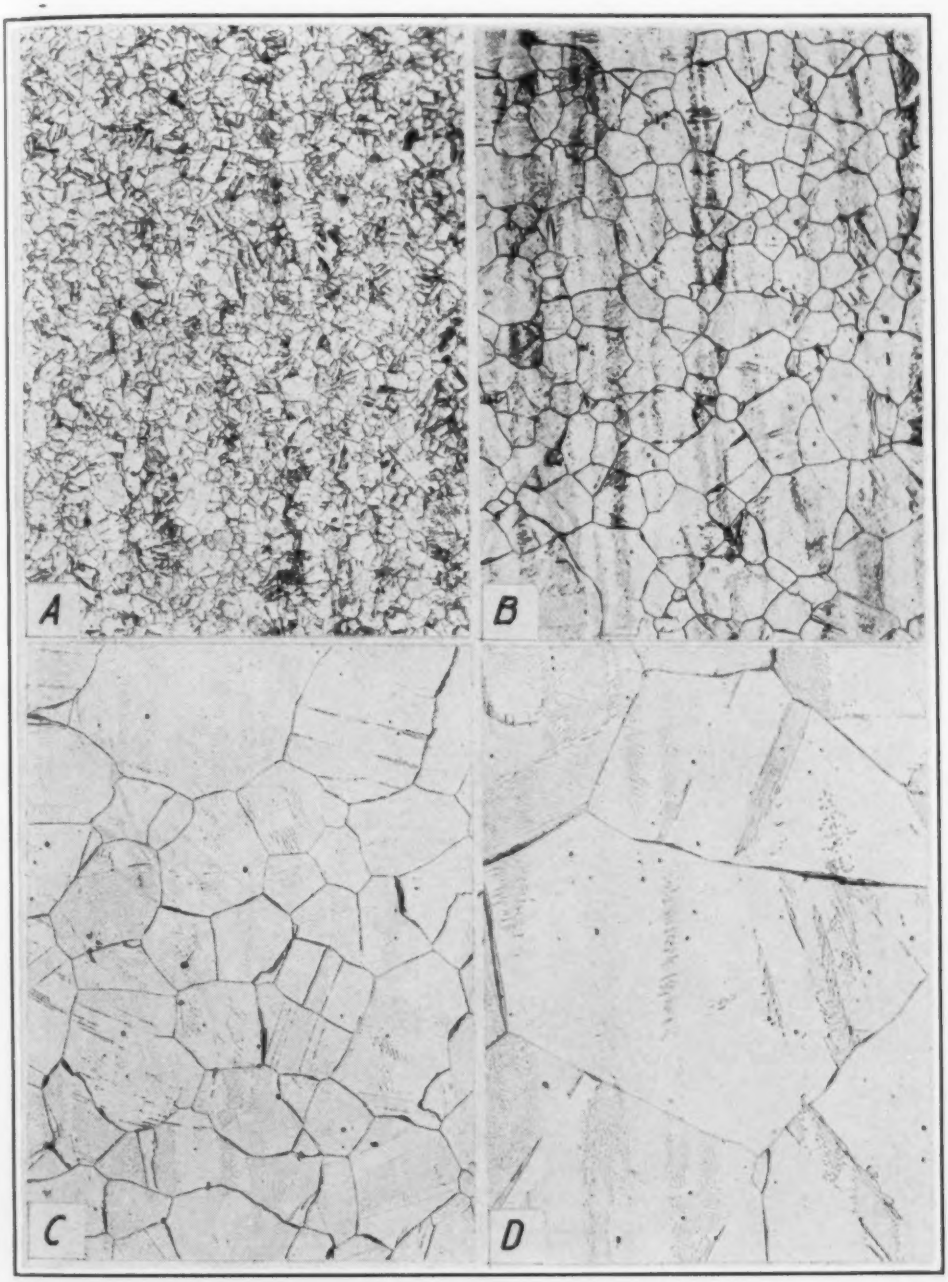


Fig. 15—Photomicrographs of Grain Size of 0.05 Per Cent Carbon, "18-8" Alloy, After Reheating 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.). Etched with Hydrochloric Acid and Ferric Chloride. × 100. A—"Hot-Rolled," Brinell 156. B—1900-Degree Fahr. (1040 Cent.) Quench, Brinell 153. C—2100-Degree Fahr. (1150 Degrees Cent.) Quench, Brinell 143. D—2300-Degree Fahr. (1260 Degrees Cent.) Quench, Brinell 137.

Fahr. (425 to 925 degrees Cent.) consequently, and, in view of some previous work in this direction, a selection has been made of 1200

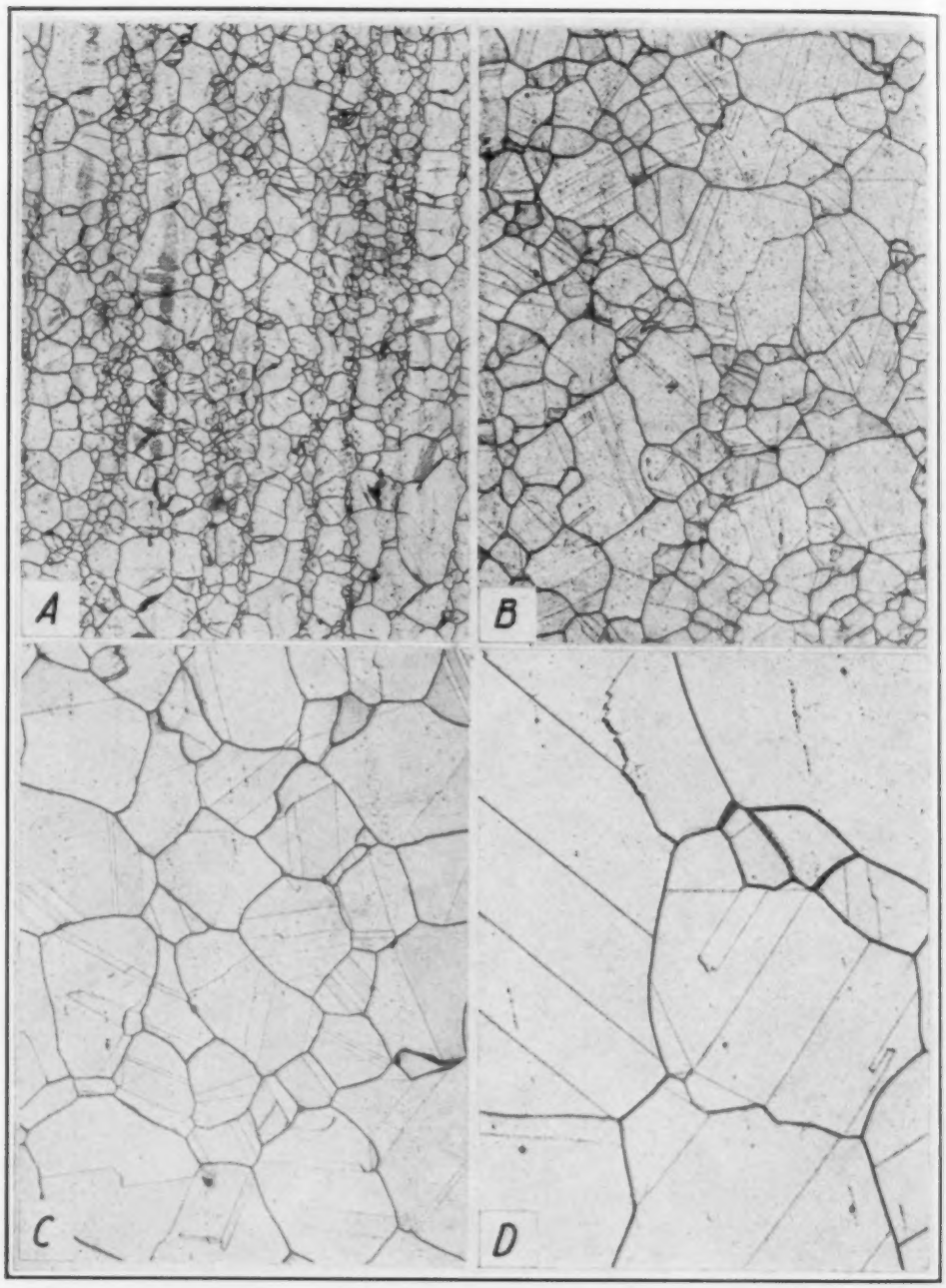


Fig. 16—Photomicrographs of Grain Size of 0.14 Per Cent Carbon, "18-8" Alloy, after Reheating 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) Etched with Hydrochloric Acid and Ferric Chloride. × 100. A—"Hot-Rolled," Brinell 170. B—1900-Degree Fahr. (1040 Degrees Cent.) Quench, Brinell 156. C—2100-Degree Fahr. (1150 Degrees Cent.) Quench, Brinell 146. D—2300-Degree Fahr. (1260 Degrees Cent.) Quench, Brinell 130.

degrees Fahr. (650 degrees Cent.) to illustrate the behavior of the alloy under 150 hours heating. It should be here noted, that heating

the alloys at 800 degrees Fahr. (425 degrees Cent.) which temperature is below that producing carbide precipitation, or heating at 1600 degrees Fahr. (870 degrees Cent.), for example, will not produce changes in structure which are equivalent with the changes effected by heating at the selected temperature, 1200 degrees Fahr. (650 degrees Cent.). In other words, the changes produced will correspond to the particular temperature to which the alloy was heated, and, in consequence, the structures shown are representative of heating at the selected temperature only.

The structures of the hot-rolled and heat treated alloys, after heating 150 hours at 1200 degrees Fahr. (650 degrees Cent.), are shown in Figs. 15 and 16. The specimens from which these photomicrographs were taken were not from failed tensile pieces, but from separate specimens which were heated the 150 hour period along with the tensile specimens during treatment at 1200 degrees Fahr. (650 degrees Cent.).

A study of these structures, compared with the unheated alloy, reveals that no change in grain size has taken place. The grain boundaries are much more easily etched and they have assumed a rounded, less angular appearance giving rise to a pebbly effect, especially in the hot-rolled alloy. Due to loss in corrosion resistance, the grain boundaries in the reheated alloys appear broader than in the unheated alloys because of the more pronounced attack of the etching reagent.

The Brinell hardness of the reheated alloys has increased slightly by the phenomena of precipitation hardening and simple qualitative tests indicate the alloys have become slightly magnetic due to separation of alpha iron. This latter effect appears somewhat more pronounced in the 0.05 per cent carbon than in the 0.14 per cent carbon alloy.

Corrosion Resistance After Heating

The influence of carbide precipitation, on the corrosion resistance of the chromium-nickel austenitic steels, has been pointed out by: Strauss, Schottky and Hinnueber,[10] Aborn and Bain,[11] in which the

[10]B. Strauss, H. Schottky and J. Hinnueber, "Carbide Precipitation During Tempering of Corrosion Resistant Non-Magnetic Chromium-Nickel Steel," *Zeitschrift fuer Anorganische und Allgemeine Chemie.* Vol. 188, January, 1930.

[11]R. H. Aborn and E. C. Bain, "The Nature of the Nickel-Chromium Rustless Steels," Transactions of the American Society for Steel Treating. Vol. 18, p. 837.

mechanism of intergranular corrosion is described. Pilling[12] has also described tests on corrosion embrittlement in a recent article.

The author has observed that the heating resulting from welding and service at certain elevated temperatures may cause intergranular corrosion, especially in the higher carbon content 18-8 alloys.

The general effect of reheating on corrosion resistance of heat

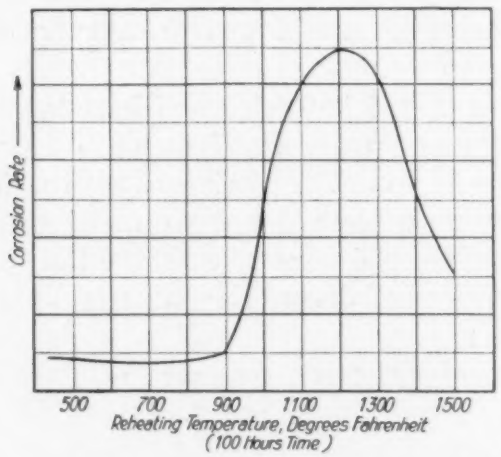


Fig. 17—Effect of Reheating on Corrosion Rate, 2150 Degree-Fahr. (1175 Degrees Cent.) Quench, 0.10 Per Cent Carbon "18-8" Alloy.

treated 0.10 per cent carbon alloy is shown in Fig. 17. This curve depicts the change in corrosion rate on reheating 100 hours at various temperatures using 10 per cent boiling sulphuric acid as a testing medium. The measurement of corrosion rate, on reheating within the carbide precipitation range, cannot be accurately determined because, while some of the weight loss results from general solution of the alloy, the majority of the attack is of an intercrystalline nature. Continual grain dislodgment occurs while specimens are being washed and handled, and, unless all grains corroded around their boundaries are removed, the loss in weight per unit time is not a correct revelation of the injury done.

A number of tests such as described above indicate that the most pronounced injury or embrittlement occurs in 18-8 alloys when they are subjected to corrosion after reheating in a temperature range 1000 to 1450 degrees Fahr. (540 to 790 degrees Cent.). This is assumed

[12]Norman B. Pilling, "Some Effects of Nickel Content in Austenitic Iron-Chromium-Nickel Alloys," *Proceedings*, American Society for Testing Materials, Vol. 30, Part II, 1930, p. 278.

Table VI

Corrosion Test in 10 Per Cent Boiling Sulphuric Acid After Reheating 150 Hours at 1200 Degrees Fahr.

Condition	0.05 Per Cent Carbon 18-8	0.14 Per Cent Carbon 18-8
Hot-rolled	0.2438	1.901
1900 Degrees Fahr., quenched	0.7666	1.260
2100 Degrees Fahr., quenched	0.0712	1.100
2300 Degrees Fahr., quenched	0.0514	1.430

Note: Figures denote loss in grams per square inch per hour. Duration of test, three hours. Samples of equal exposed surface area.

to be due to precipitation of finely dispersed carbides[13] within this temperature range which causes depletion of chromium in the vicinity of boundaries and reparation by diffusion cannot occur because of the low temperatures. Reheating at temperatures lower than 1000 degrees Fahr. (540 degrees Cent.) results in no damage because of insufficient precipitation while reheating at temperatures higher than 1450 degrees Fahr. (790 degrees Cent.) causes coalescence of the carbides into larger globules with reparation of the chromium depleted boundaries by diffusion from within the grains themselves. This results in a partial recovery of corrosion resistant properties.

The 18-8 alloy, containing above approximately 0.07 per cent carbon, which has been reheated at temperatures between 1110 to 1290 degrees Fahr. (600 to 700 degrees Cent.) is rapidly embrittled when boiled in a solution containing 10 per cent sulphuric acid and 10 per cent copper sulphate. This test was devised by Strauss and is now familiarly known as the "Strauss Embrittlement Test." It has been found that other corrosive agents such as, sulphuric acid, sulphuric acid and ferric sulphate, acetic acid, hot salt water and even tap water, on long periods of exposure, can cause intergranular corrosion of 18-8 alloy which has been reheated at these temperatures.

In the presence of corrosion and in combination with stress, chromium-nickel austenitic alloys, which have been reheated to a temperature sufficient for fine carbide precipitation, may fail rapidly. Numerous cases of such failures have been noted, particularly in welded parts which have not been heat treated subsequent to the welding operation. Disregarding the influence of stress (which admittedly has a great effect) the author sees a great deal in common between the corrosion occurring after such reheating and the corrosion which

[13]The composition of the carbides which precipitate is unknown, but experiments by Aborn and Bain indicate that the chromium content of these carbides is very high, probably in the vicinity of 90 per cent chromium. (See reference 11.)

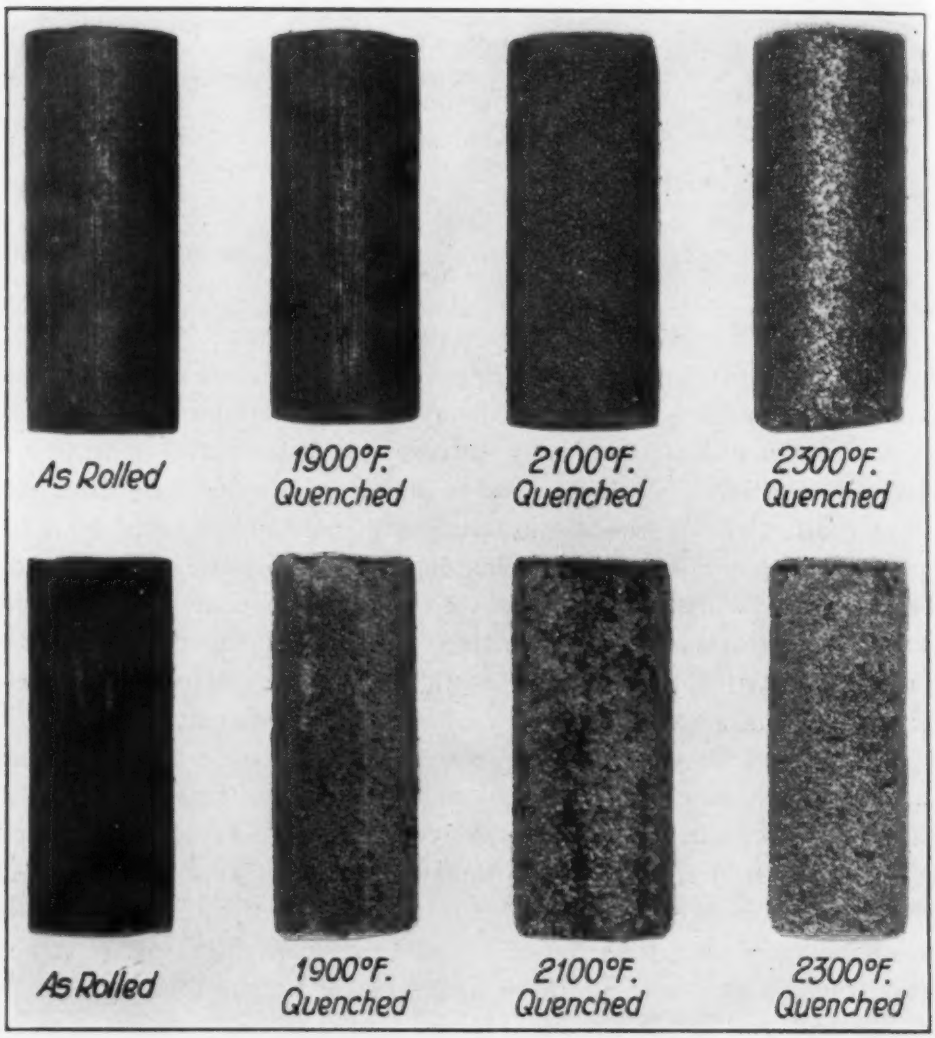


Fig. 18—Photographs of Corrosion Test Specimens of: (a) 0.05 Per Cent Carbon Alloy, (b) 0.14 Per Cent Carbon Alloy, Reheated 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) and then Immersed 3 Hours in 10 Per Cent Boiling Sulphuric Acid. Original Heat Treatments or Condition Given Above. Photographs About Actual Size.

might occur while the alloy is maintained within the fine precipitation range at elevated temperatures.

Accordingly, corrosion tests were made on the 0.05 and 0.14 per cent carbon alloys in the hot-rolled and heat treated conditions, after reheating 150 hours at 1200 degrees Fahr. (650 degrees Cent.). Boiling 10 per cent sulphuric acid was selected as the testing medium because of its rapid rate of attack and its reducing action. Test results are contained in Table VI, but, as previously pointed out, loss in weight is not a true indication of the damage resulting from re-

heating, consequently, the results should be viewed as an approximation only. It is obviously better to have a general diminishing of corrosion resistance with little or no intergranular attack, than to have definite intergranular corrosion which could be construed as making the alloy part quite unreliable under conditions of stress at either low or elevated temperatures. Further consideration of the corrosion rates shown is unnecessary because a slight loss representing grain boundary corrosion is much more detrimental than a relatively larger loss in weight representing surface attack. From the photograph of the corrosion test specimens in Fig. 18, it may be observed that the initial heat treatment materially affects the susceptibility to intergranular corrosion attack after reheating at 1200 degrees Fahr. (650 degrees Cent.). It will be observed that the hot-rolled and 1900 degrees Fahr. (1040 degrees Cent.) quenched 0.05 per cent carbon alloy have retained their characteristics, there being no intergranular attack on the hot-rolled and only slight intergranular attack on the 1900 degrees Fahr. (1040 degrees Cent.) quenched alloy. In the 2100 and 2300 degrees Fahr. (1150 and 1260 degrees Cent.) quenched 0.05 per cent carbon alloy, intergranular attack has occurred and grains of the alloy may be readily detached from either specimen by picking with the fingers. In the 0.14 per cent carbon alloy all conditions are affected by intergranular corrosion and in a greater degree than the lower carbon alloy. The hot-rolled 0.14 per cent carbon corrosion test specimen has the appearance of surface corrosion because of its fine grain size, but it has also suffered intergranular attack. The corrosion test specimens employed for this test were cut adjacent to each other from bars of each alloy before their respective heat treatments and the reheating at 1200 degrees Fahr. (650 degrees Cent.). It is evident that the only variable affecting the intergranular corrosion of each alloy was the grain size of the individual specimens as induced by the initial heat treatment. The apparatus used for the corrosion tests consisted of a flask equipped with a reflux condenser substantially the same as that described by Huey.[14]

Intergranular Attack

Having established that intergranular corrosion in 18-8 alloys, on

[14]William R. Huey, "Corrosion Test for Research and Inspection of Alloys," Transactions of the American Society for Steel Treating, Vol. 18, 1930, p. 1126.

reheating within the carbide precipitation range, is a function of both carbon content and grain size, it becomes of interest to measure the degree of susceptibility as influenced by these factors. This was attempted by cutting the corrosion test specimens shown in Fig. 18 transversely, followed by polishing and examining microscopically, the corroded edges of the specimens. This examination brought out the findings, that in the absence of stress, the intergranular attack proceeded to remove one, or, at the most, two layers of grains at a time by boundary corrosion. The larger grained alloys, of course, suffered most by such process as one layer of large grains might equal three or four or more layers of smaller grains. All but the "hot-rolled" and 1900 degrees Fahr. (1040 degrees Cent.) quenched 0.05 per cent carbon 18-8 alloy had suffered by the mode of attack described.

The edge sections of the corrosion tests showed only one or two layers of grains attacked, consequently, the actual amount of attack in a given time in the individual specimens could only be determined by reference to original diameter of the specimens. Instead of this measurement, the transversely cut specimens were polished on their cross sections, as for a microscopic examination and then subjected to the Strauss solution consisting of boiling 10 per cent sulphuric acid and 10 per cent copper sulphate.

Copper sulphate, when added to solutions of sulphuric acid[15] acts as a passivifying agent and prevents the attack on stainless alloys which occurs in straight sulphuric acid solutions. This is true, however, only when the alloys are in the proper condition for corrosion resistance. If certain areas are affected, for example, the grain boundary areas of austenitic nickel-chromium-iron alloys, by reheating in the carbide precipitation range, an impoverishment of chromium at these areas takes place and the protective film giving corrosion resistance is no longer maintained. This allows local corrosion to proceed so that the Strauss solution becomes a very excellent means of showing local impairment of corrosion resistant properties at the grain boundaries of reheated 18-8 alloys.

The reheated 0.14 per cent carbon alloy showed considerable attack on the polished surfaces of the corrosion test specimens on two hours immersion in boiling Strauss solution. This attack proceeded by way of grain boundary corrosion, which allowed whole

[15] J. G. H. Monypenny, "Stainless Iron and Steel," John Wiley & Sons, Inc., 1926, p. 187.

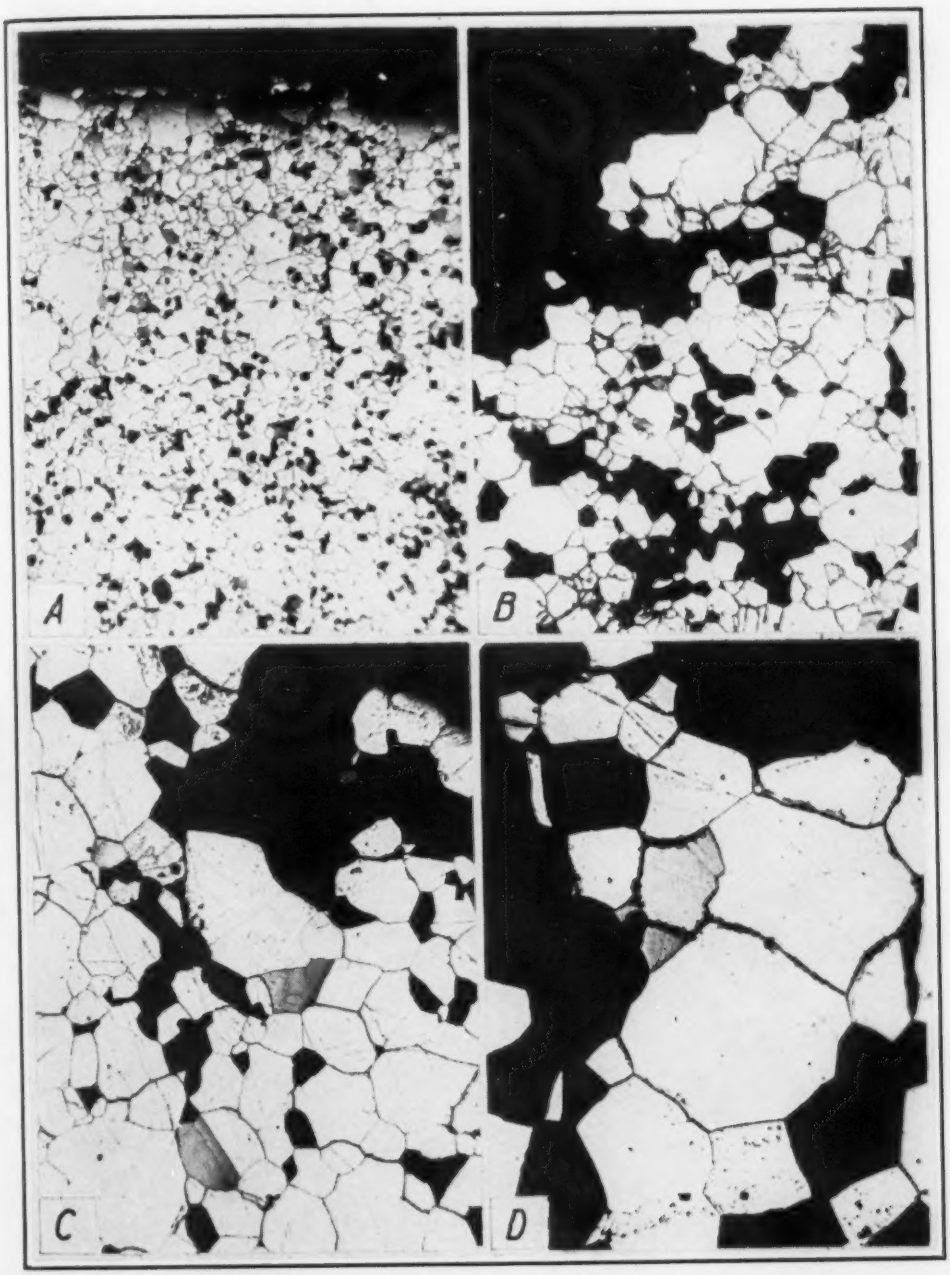


Fig. 19—Photomicrographs of Polished Corrosion Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, Reheated 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) and Boiled 2 Hours in "Strauss Solution." × 50. A—"Hot-Rolled." B—1900-Degree Fahr. (1040 Degree Cent.) Quench. C—2100-Degree Fahr. (1150 Degree Cent.) Quenched. D—2300-Degree Fahr. (1260 Degree Cent.) Quench.

grains to be dislodged from both the edges and surface of the specimens. The grains themselves seemingly maintained their corrosion resistance, but large quantities of practically perfect austenite grains

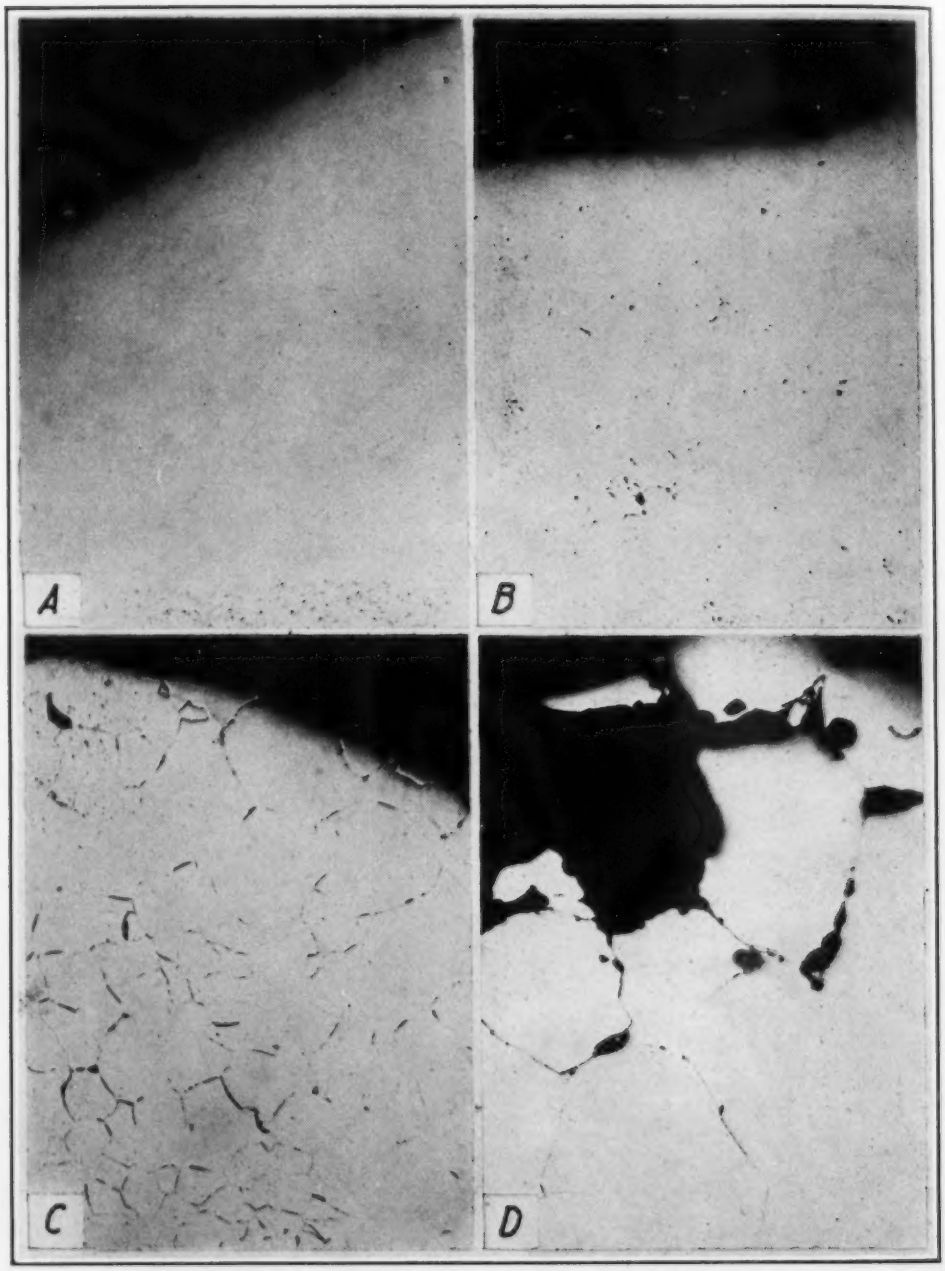


Fig. 20—Photomicrographs of Polished Corrosion Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, Reheated 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) and Boiled 10 Hours in "Strauss Solution." × 50. A—"Hot-Rolled." B—1900-Degree Fahr. (1040 Degree Cent.) Quench. C—2100-Degree Fahr. (1150 Degree Cent.) Quench. D—2300-Degree Fahr. (1260 Degree Cent.) Quench.

were removed from the parent metal. The positions occupied by grains before their removal from the specimens may be seen in the photomicrographs of the corrosion specimens contained in Fig. 19.

The darkened heavy grain boundaries represent corrosion and the blackened grains represent, in some cases, dislodgment of grains leaving holes in the surface and, in other cases, staining by precipitated copper, which resulted from impairment of corrosion resistance. In the 0.14 per cent carbon alloy, the amount of attack was considerable for all grain sizes, but was much greater in the larger grained material.

The reheated 0.05 per cent carbon alloy, by virtue of its lower carbon content and, consequently, smaller amount of precipitated carbides showed only a small amount of corrosion in the 2100 and 2300 degrees Fahr. (1150 and 1260 degrees Cent.) quenched conditions, after two hours immersion in boiling Strauss solution, and showed practically no corrosion in the "hot-rolled" and 1900 degrees Fahr (1040 degrees Cent.) quenched condition. Boiling was continued for a total of 10 hours, after which the photomicrographs in Fig. 20 were taken.

It will be observed that only a small amount of intergranular attack has occurred on the 2100 and 2300 degrees Fahr. (1150 and 1260 degrees Cent.) quenched 0.05 per cent carbon alloy, and none has occurred on the "hot-rolled" and 1900 degrees Fahr. (1040 degrees Cent.) quenched alloy. No grains have been dislodged in the finer-grained conditions and no copper staining is evident, indicating that corrosion resistance has not been diminished. The grain boundaries have been etched slightly wherever carbide has formed, but due to the slight amount precipitated, a discontinuous net work prevents intergranular attack from surrounding the grains.

Carbide Precipitation and Grain Boundary Extent

Krivobok and Grossmann,[16] discuss the influence of carbide precipitation on reheating the 18-8 type alloy, while Aborn and Bain[11] and Strauss and co-workers[10] point out that carbide precipitation occurs mainly at grain boundaries. Precipitation may also occur at "twinnings", or at slip planes in worked metal, or, to some extent, throughout the grains themselves.

Disregarding (for the purpose of simplicity) carbide precipitation occurring at any points except at grain boundaries, it imme-

[16] V. N. Krivobok and M. A. Grossmann, "Influence of Nickel on the Chromium-Iron-Carbon Constitutional Diagram," Transactions, American Society for Steel Treating, Vol. IX, 1930, p. 808. See also joint discussion of this paper and reference 11, "Rustless Steels," p. 873.

diately becomes apparent that the amount or "extent" of grain boundaries available to the precipitated carbides, as well as carbon content, will govern the corrosion resistant properties of the alloy after such precipitation has occurred. Assuming a given carbon content in an alloy and several conditions of grain size, it will be seen in Fig. 21, which represents cross-sections through a metal exactly as

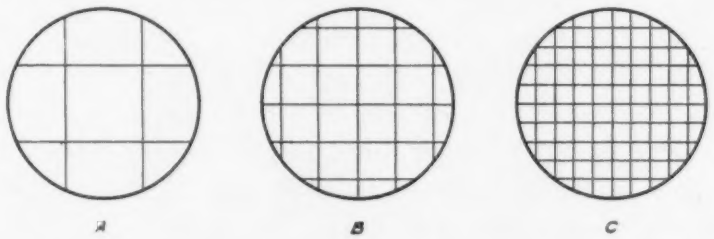


Fig. 21—Diagrammatic Sketch Showing Relationship of Grain Size to "Grain Boundary Extent" in a Metal in 3 Conditions of Grain Size.

one would view them under the microscope, that the grain boundary extent is inversely proportional to grain size.

With a large grain size, the boundary extent is considerably reduced as compared to a small grain size, consequently, precipitation of fine carbides, even in an alloy of low total carbon content, may be sufficient to cause impairment of grain boundary areas by providing enough connected carbide precipitation to permit intergranular attack under suitable conditions of corrosion. However, if the grain size is small, the carbides have plenty of available boundary space for precipitation and may even have more than sufficient for the contained carbon content. The precipitated carbide particles and regions of impoverishment may then be scattered or so widely spaced that the grains are not completely surrounded. Subsequent corrosion cannot then proceed from one grain to another or totally around a grain, consequently, intergranular corrosion cannot take place. The proof of this theory is demonstrated by the corrosion tests in both sulphuric acid and the Strauss solution.

With the 0.14 per cent carbon alloy, the amount of carbide precipitated is sufficient to completely fill the grain boundaries available, even in fairly fine-grained alloy and, therefore, intergranular corrosion cannot ordinarily be entirely eliminated by anything short of a heat treatment which will either place the carbides in solution, or coalesce the carbides into larger particles and repair the boundary areas by diffusion.

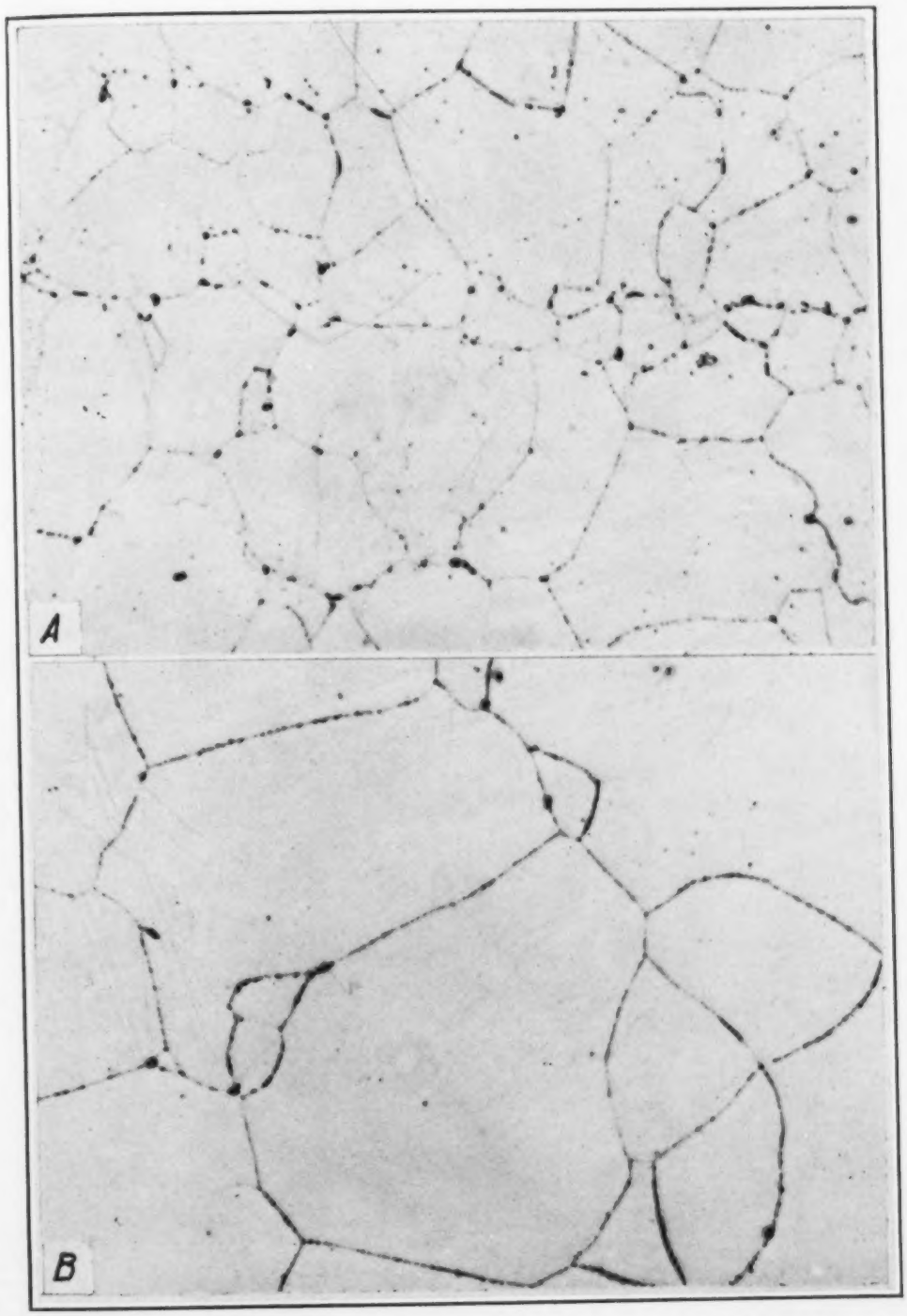


Fig. 22—Photomicrographs Showing Carbide Precipitation in (A) "Hot-Rolled" and (B) 1900-Degree Fahr. (1040 Degree Cent.) Quench 0.14 Per Cent Carbon "18-8" Alloy After Reheating 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) Etched with Murakami's Reagent. × 750.

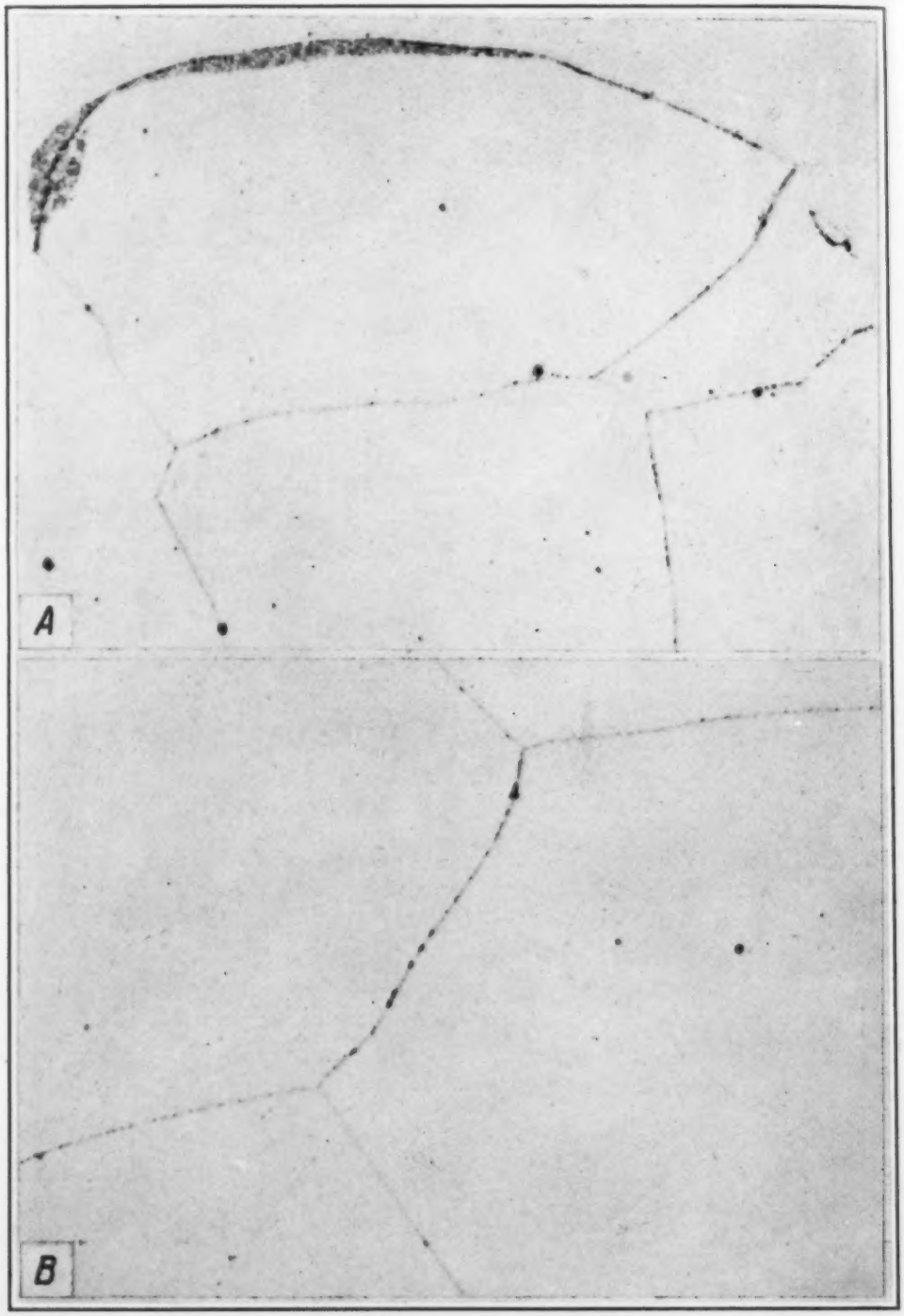


Fig. 23—Photomicrographs Showing Carbide Precipitation in (A) 2100-Degree Fahr. (1150 Degree Cent.) Quench and (B) 2300-Degree Fahr. (1260 Degree Cent.) Quench, 0.14 Per Cent Carbon "18-8" Alloy After Reheating 150 Hours at 1200 Degrees Fahr. Etched with Murakami's Reagent. × 750.

Fig. 24—Photomicrographs Showing Carbide Precipitation in (A) "Hot-Rolled" and (B) 1900-Degree Fahr. (1040 Degree Cent.) Quench, 0.05 Per Cent Carbon "18-8" Alloy After Reheating 150 Hours at 1200 Degrees Fahr. (650 Degrees Cent.) Etched with Murakami's Reagent. × 750.

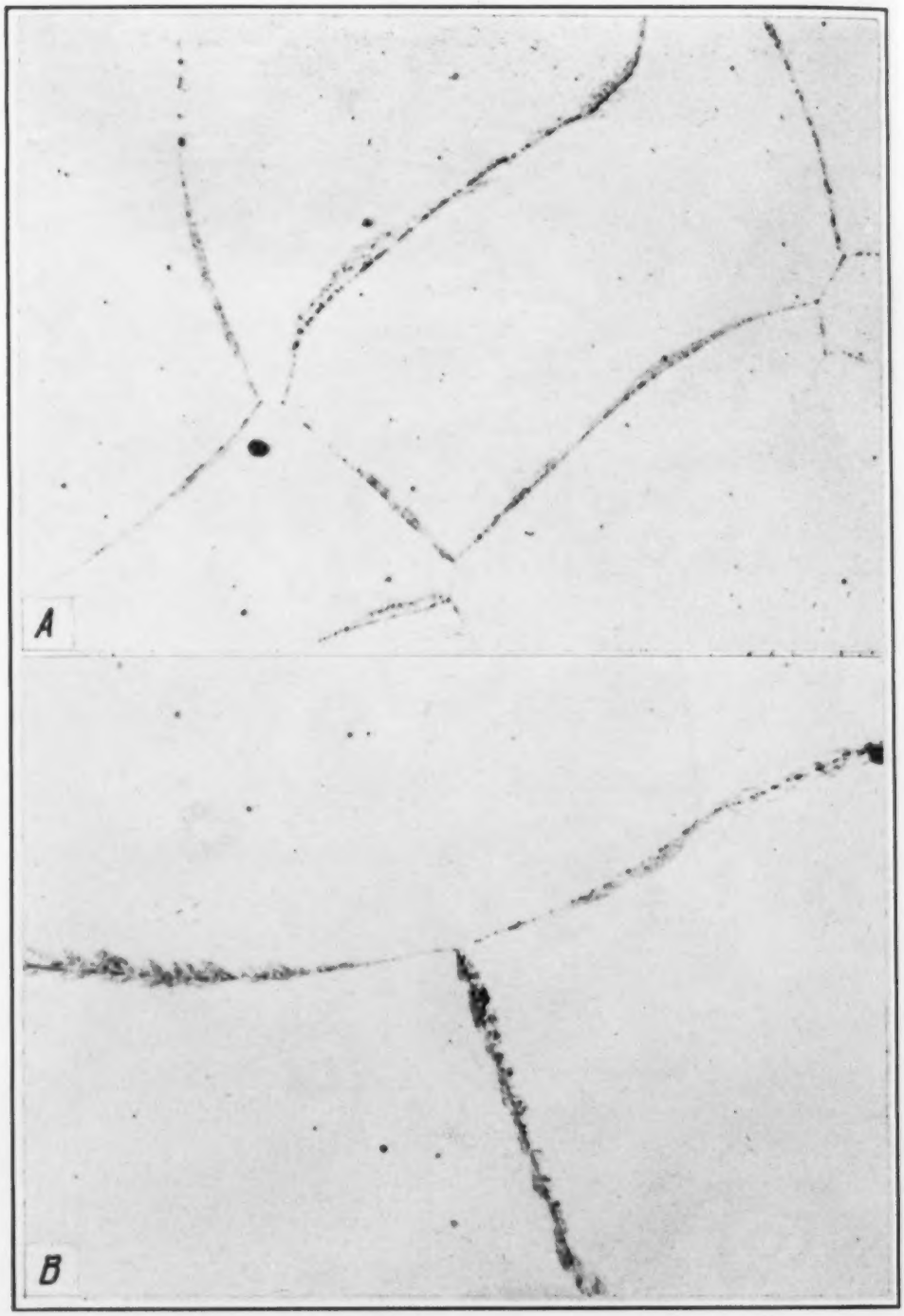


Fig. 25—Photomicrographs Showing Carbide Precipitation in (A) 2100-Degree Fahr. (1150 Degrees Cent.) Quench, and (B) 2300-Degree Fahr. (1260 Degree Cent.) Quench, 0.05 Per Cent Carbon "18-8" Alloy After Reheating 150 Hours at 1200 Degrees Fahr. Etched with Murakami's Reagent. × 750.

Possibly the ductility of the alloys at elevated temperature is also affected by the distribution of carbides at grain boundaries. The concentration of a broad band of very fine particles in the boundary regions of large-grained alloy, would be expected to interfere with ductility to a greater extent than the scattered distribution or thin band of particles present at the boundary areas in fine-grained alloy. In any event, the ductility, as determined by short time tests, bears out this conclusion.

The distribution of carbides on reheating 150 hours at 1200 degrees Fahr. (650 degrees Cent.) is shown in the photomicrographs contained in Figs. 22, 23, 24 and 25.

Summary

Preliminary experiments showing the influence of heat treatment on grain size, were made on 0.08 per cent carbon, cold drawn 18-8 alloy and on 0.056 per cent carbon, hot-rolled 18-8 alloy.

Data are presented on the short time ultimate strength and ductility of 0.05 and 0.14 per cent carbon 18-8 alloy in conditions representing several grain sizes. These data cover both one and 150 hours heating in the range 800 to 1700 degrees Fahr. (425 to 925 degrees Cent.). A discussion of the test results is given with reference to the effect of grain size on creep as found by other investigators.

The grain sizes of the alloys are shown by photomicrographs for conditions representing hot-rolled and 1900, 2100 and 2300 degrees Fahr. (1040, 1150 and 1260 degrees Cent.).

The effect of reheating at 1200 degrees Fahr. (650 degrees Cent.) on corrosion resistance, is shown by tests in dilute sulphuric acid and by susceptibility to attack in the Strauss solution.

The distribution of carbides, precipitated by reheating at 1200 degrees Fahr. (650 degrees Cent.) is shown in photomicrographs of 0.05 and 0.14 per cent carbon alloy in the hot-rolled condition and after quenching from 1900, 2100 and 2300 degrees Fahr. (1040, 1150 and 1260 degrees Cent.).

Conclusions

The following conclusions have been drawn from the results of this investigation:

The ductility of both 0.05 and 0.14 per cent carbon, 18-8 alloy, on rupture at elevated temperature, is greatly affected by the grain

size of the metal. Fine-grained alloys show much more ductility than do coarse-grained ones at temperatures in the approximate range 1100 to 1700 degrees Fahr. (595 to 925 degrees Cent.). The short time ultimate strength is also affected by grain size, but this is not considered of importance as other investigators have shown creep to be somewhat superior in coarse-grained 18-8 alloy at temperatures of 1180 degrees Fahr. (640 degrees Cent.) and above.

The corrosion resistance of 0.05 per cent carbon alloy is much less impaired by reheating within the fine carbide precipitation range than is the 0.14 per cent carbon alloy. Susceptibility to intergranular attack after reheating is influenced by both carbon content and grain size. Fine-grained low carbon alloy is not susceptible to intergranular corrosion on reheating, but may become so if the grain size is sufficiently large. This is due to the amount or extent of grain boundaries available to the precipitated carbides. The higher carbon alloy (0.14 per cent) is susceptible even in a fine-grained condition by reason of the greater amount of carbon available for precipitation.

Low carbon alloy having a fine grain size is to be preferred for elevated temperature service involving corrosion because of its greater ductility and nonsusceptibility to intergranular attack.

Restriction of the carbon content and of the grain size of the 18-8 alloy produces the most satisfactory condition for ductility at elevated temperature and for maintenance of corrosion resistant properties at or after heating to a temperature sufficient for carbide precipitation.

Acknowledgment

The author wishes to express his appreciation to the officials of the Babcock and Wilcox Tube Co. for permission to publish the data contained in this paper. The helpful suggestions of N. Hamilton are acknowledged and special credit is deserved by C. P. Church and Z. Olzak for making the many elevated temperature tests. Thanks are also due C. P. Church for preparation of the photomicrographs.

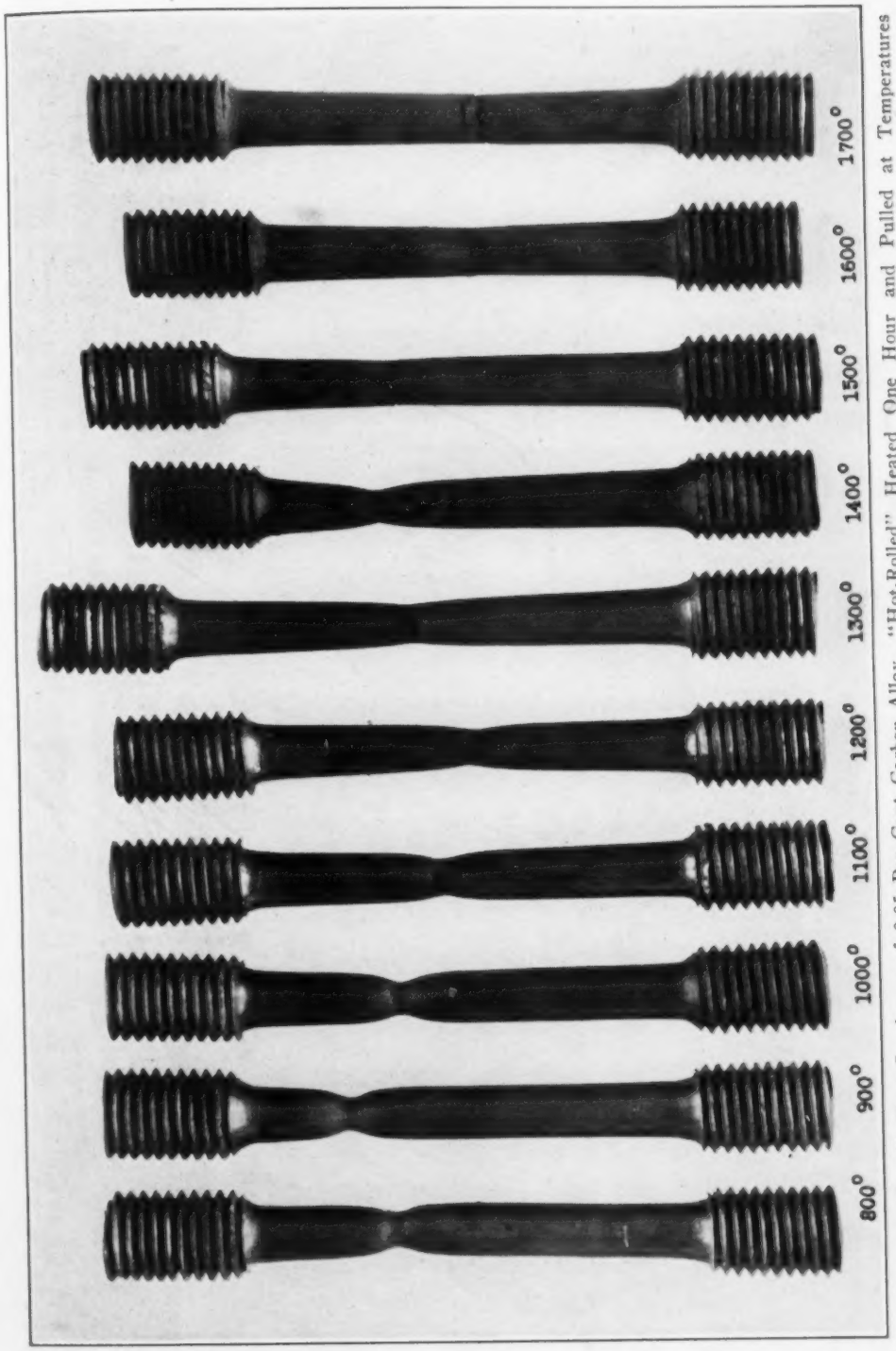


Plate 1—Tensile Test Specimens of 0.05 Per Cent Carbon Alloy, "Hot-Rolled" Heated One Hour and Pulled at Temperatures Shown.

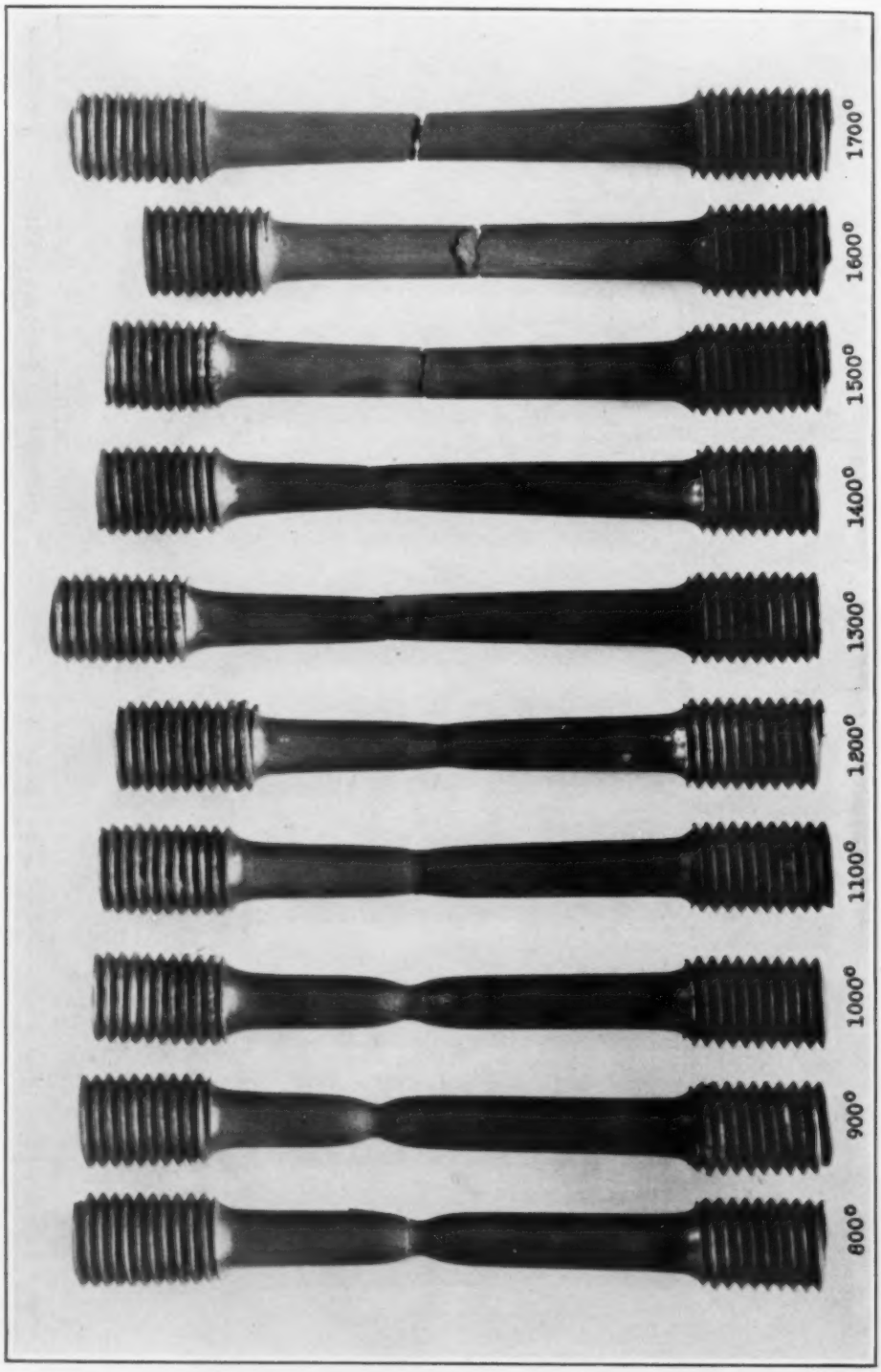


Plate 2—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

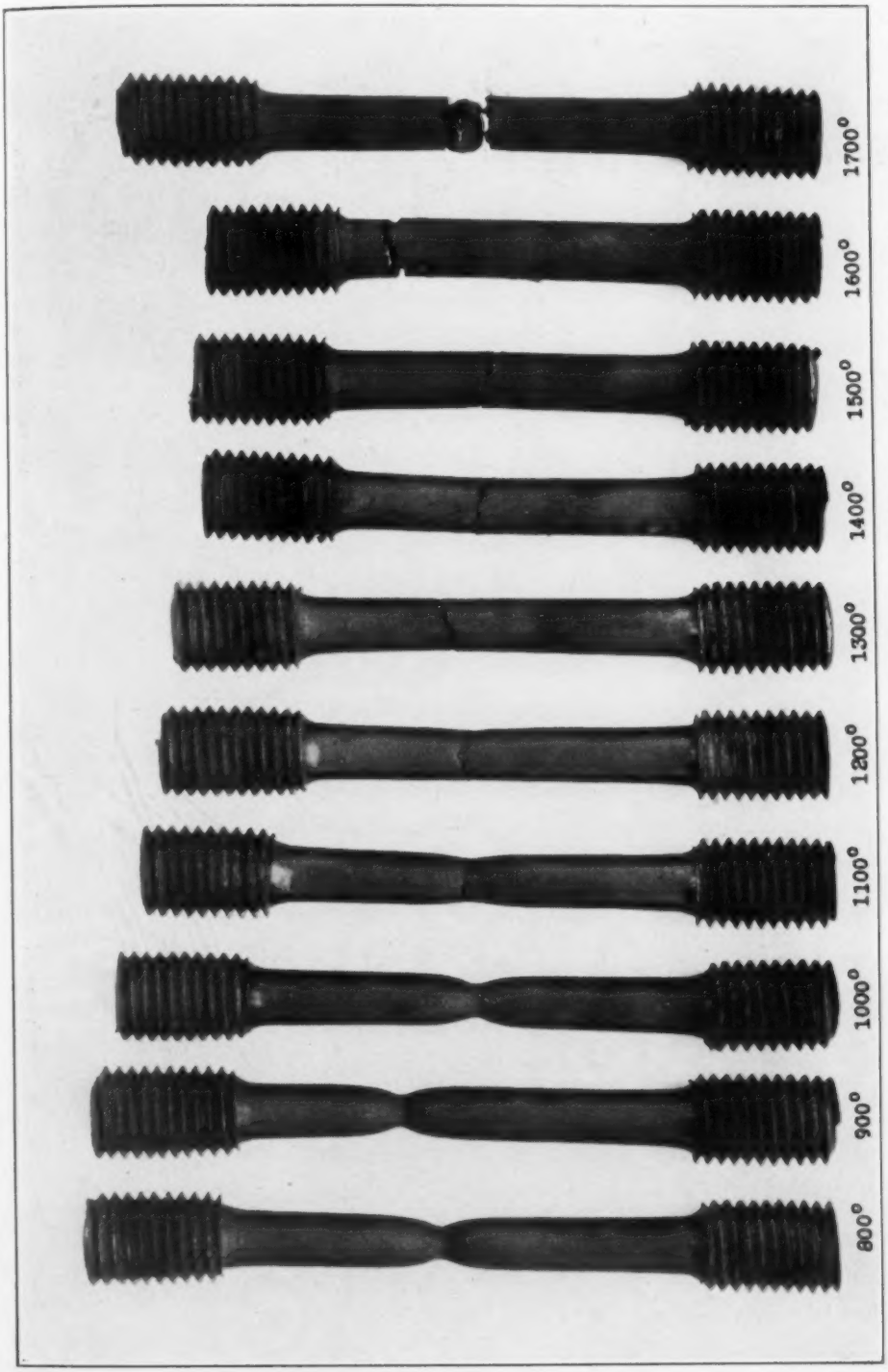


Plate 3—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 2100 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

Plate 2—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

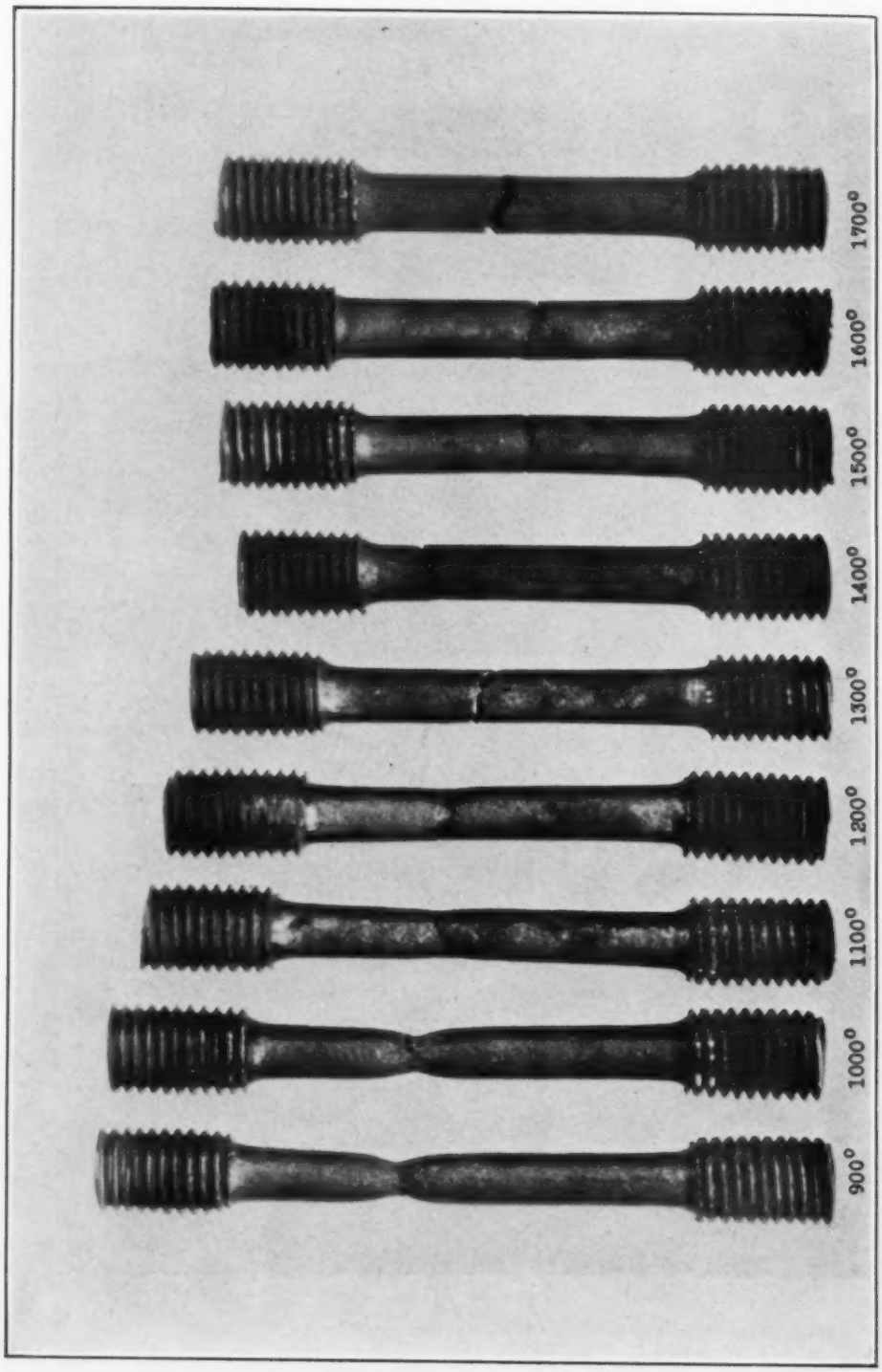


Plate 4—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

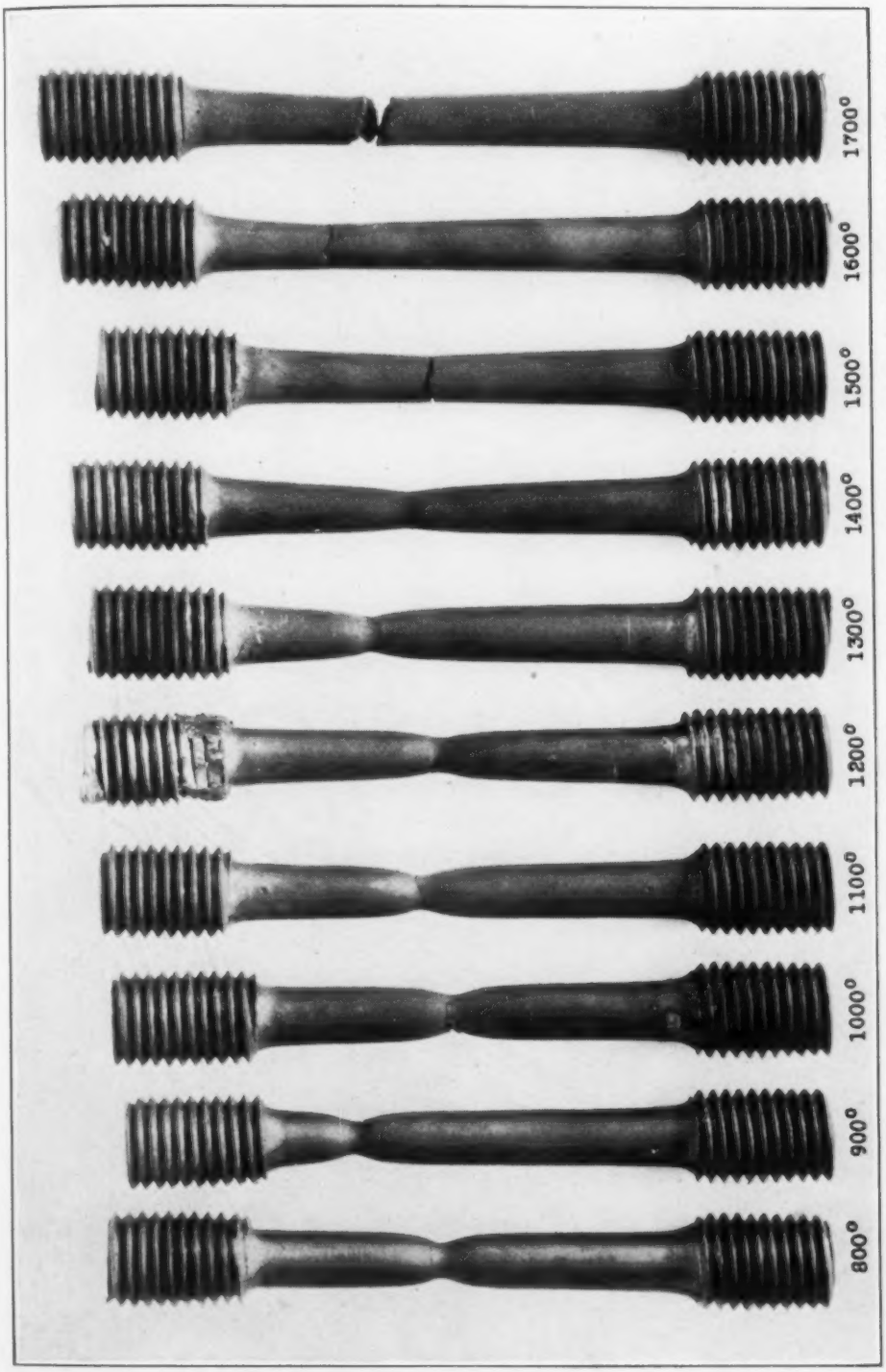


Plate 5—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, "Hot-Rolled" Heated 150 Hours and Pulled at Temperatures Shown.

Plate 4—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

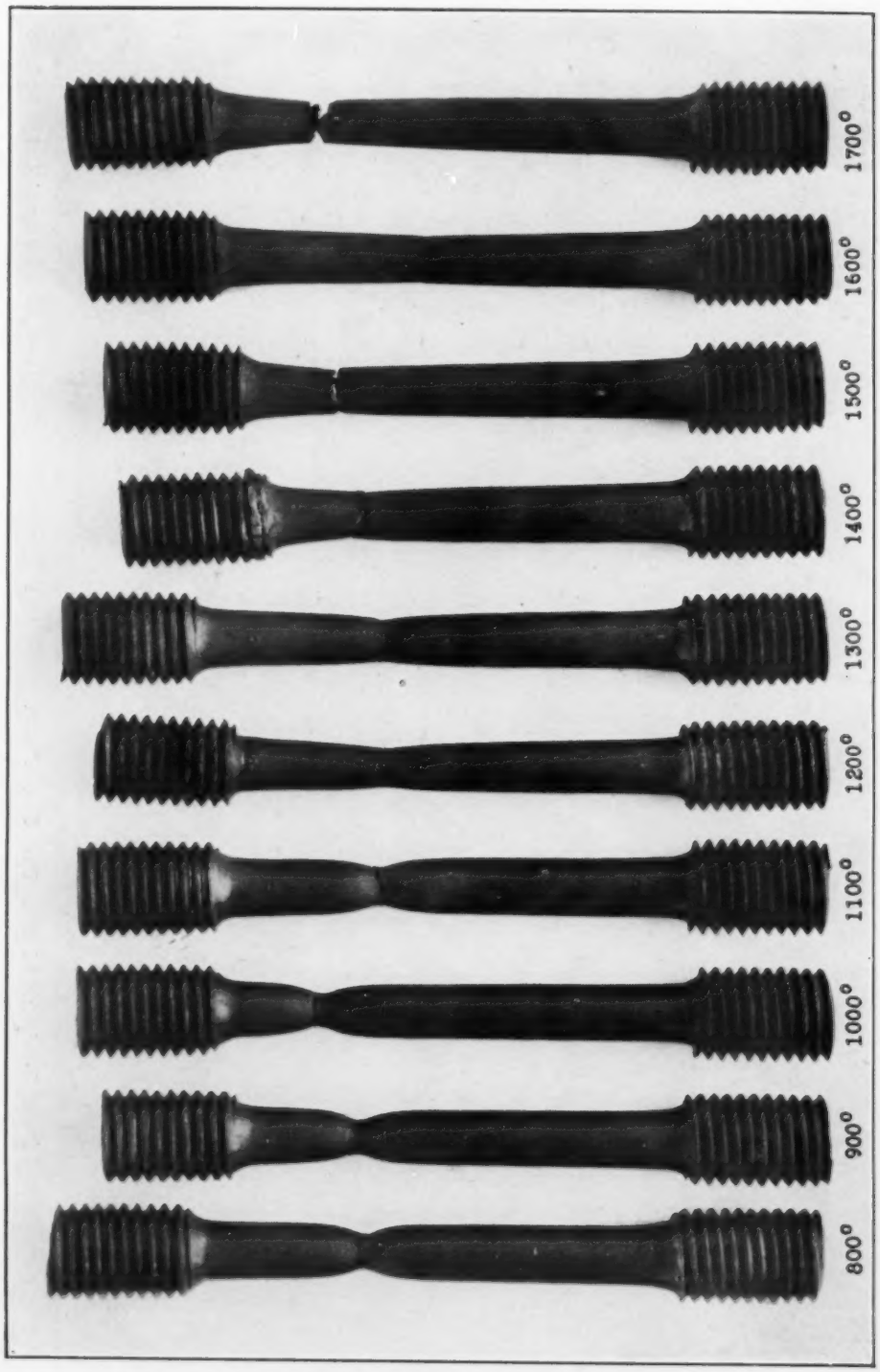


Plate 6—Tensile Test Specimens of 0.05 Per Cent Carbon "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

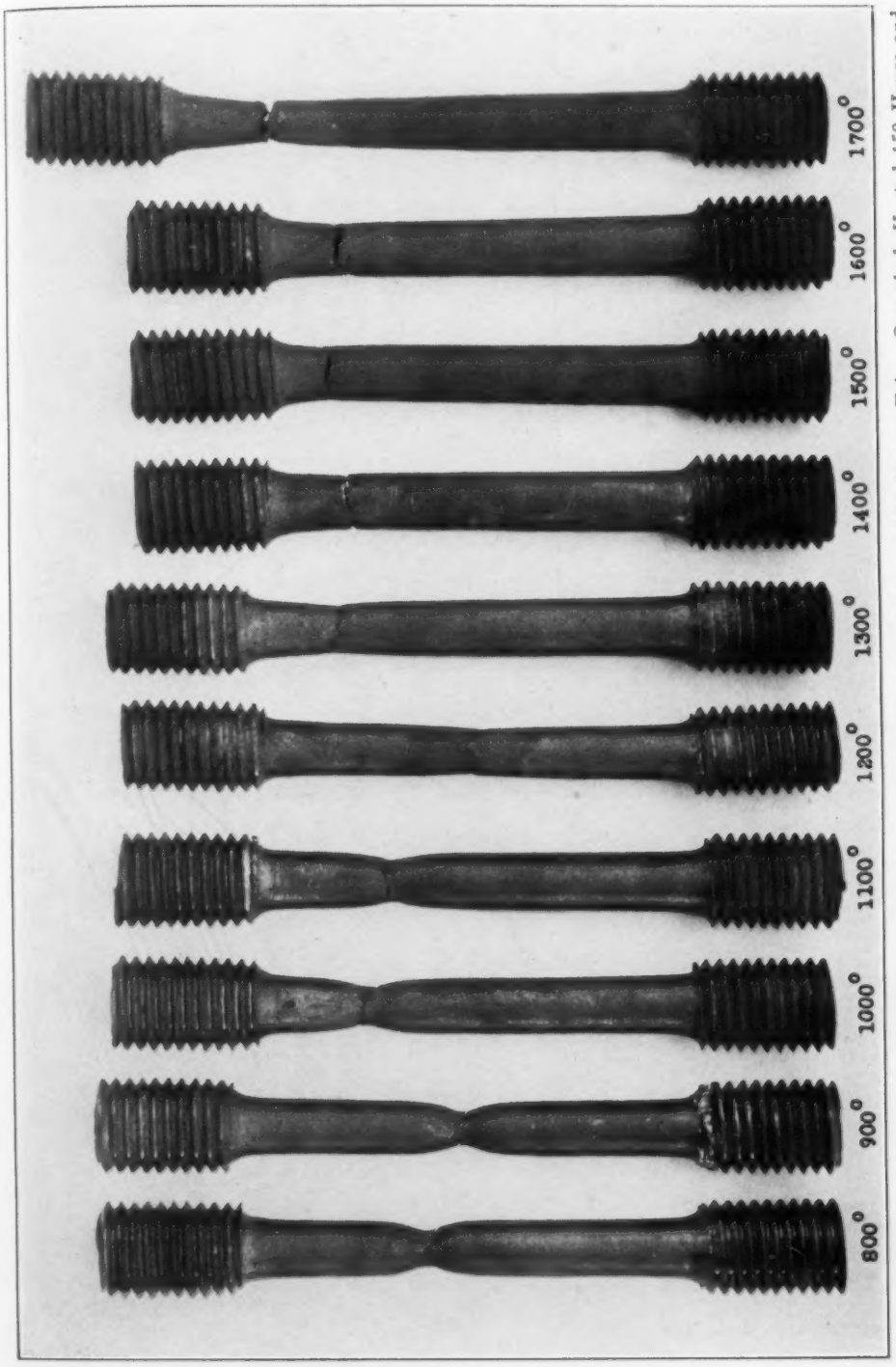


Plate 7—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 2100 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

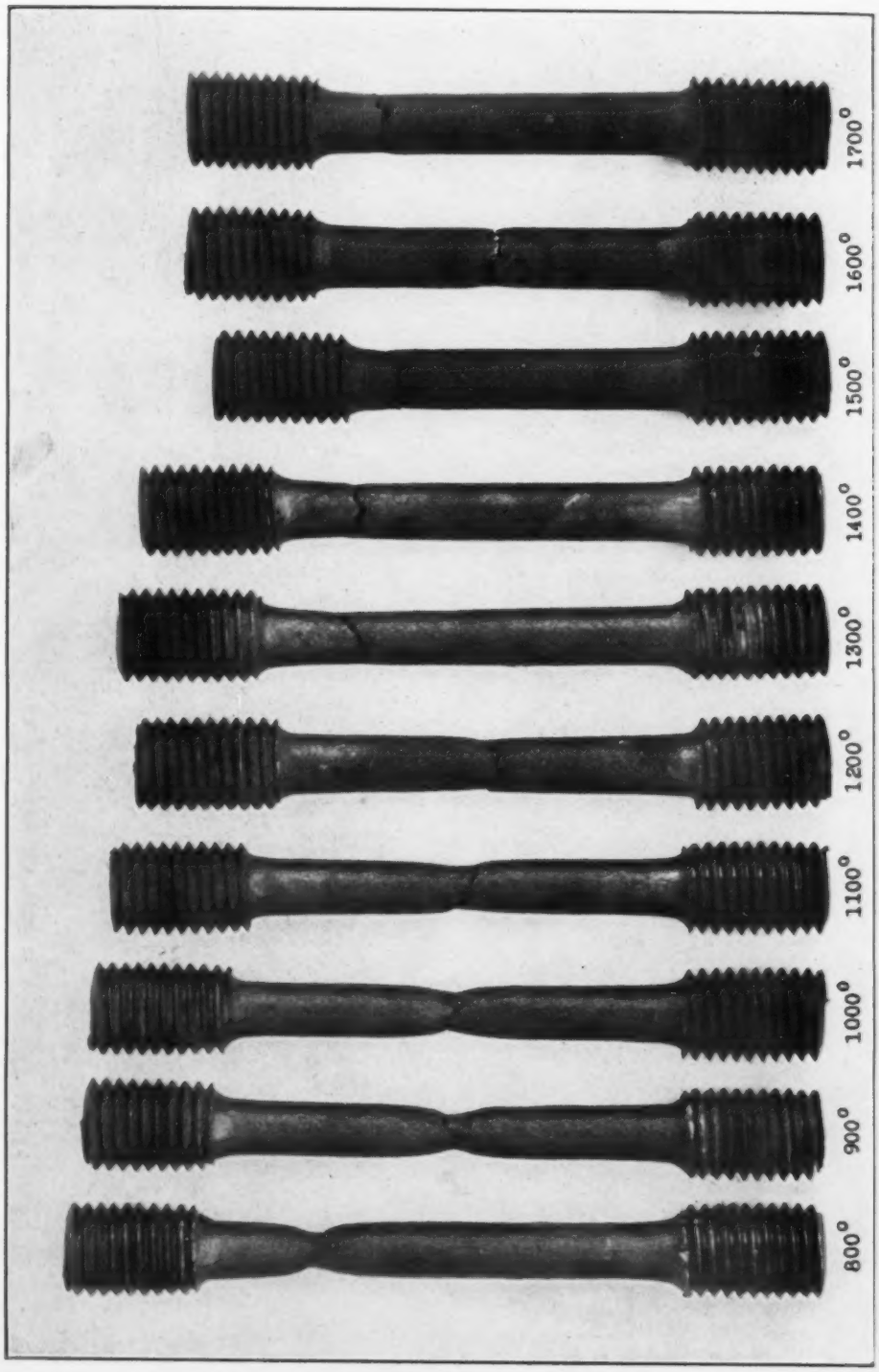


Plate 8—Tensile Test Specimens of 0.05 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

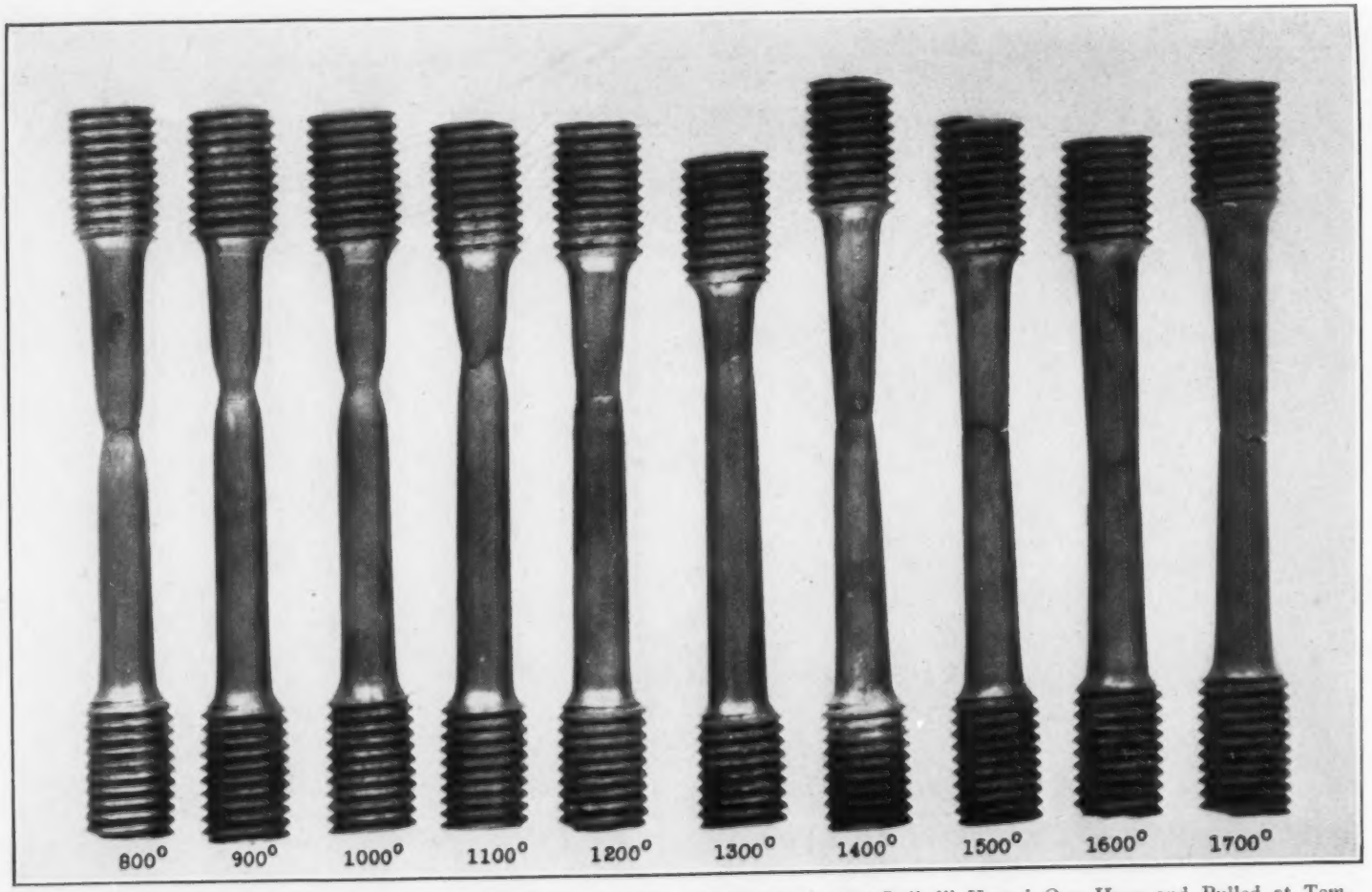


Plate 9—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, "Hot-Rolled" Heated One Hour and Pulled at Temperatures Shown.

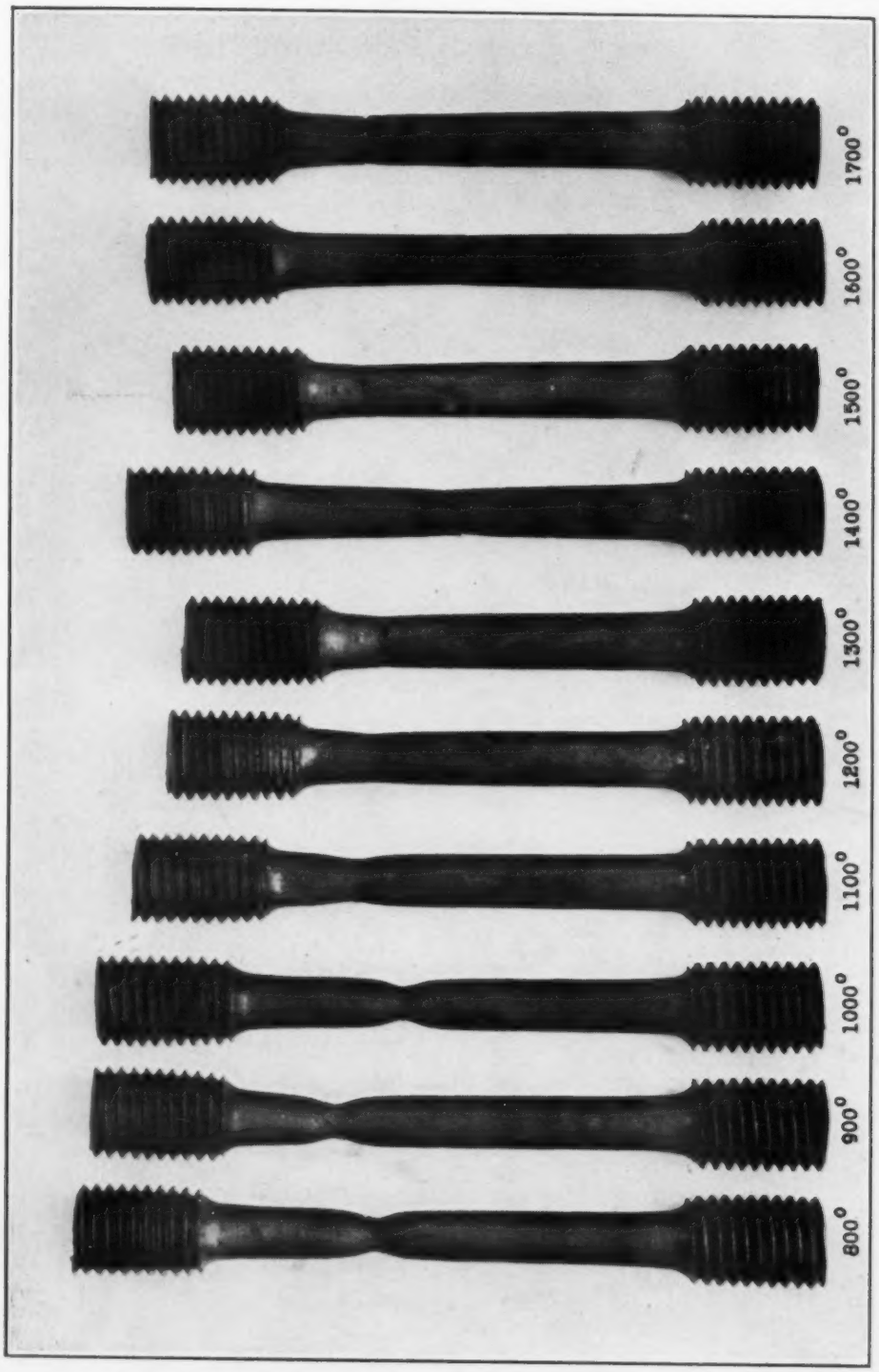


Plate 10.—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

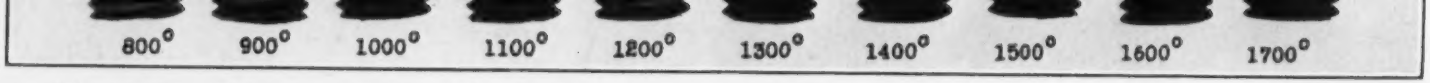


Plate 10—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

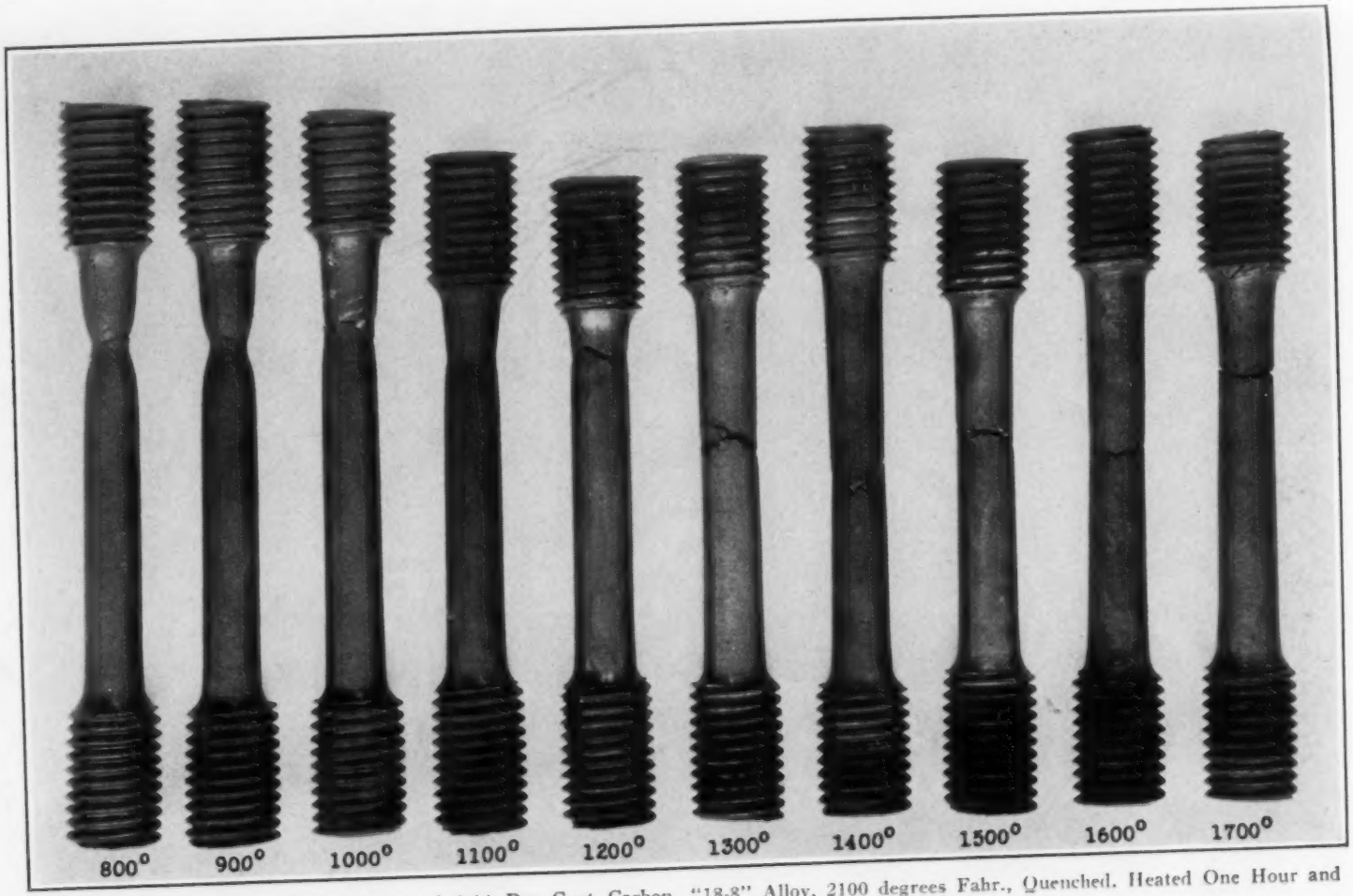


Plate 11—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2100 degrees Fahr., Quenched. Heated One Hour and Pulled at Temperatures Shown.

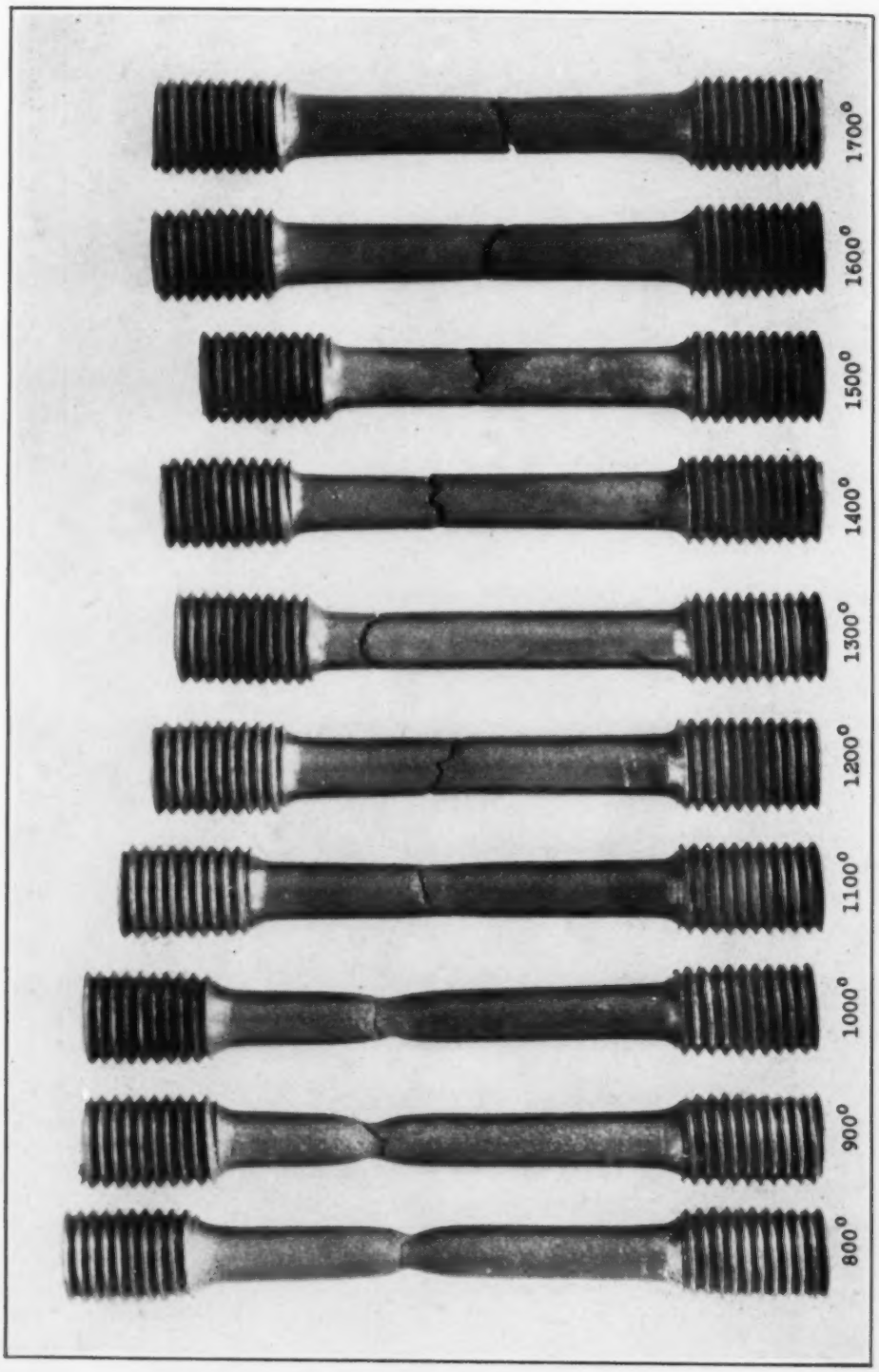


Plate 12—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

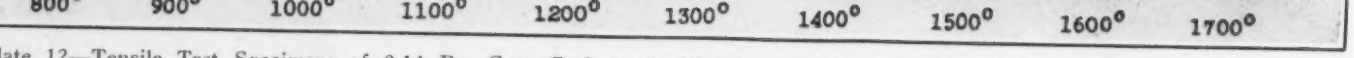


Plate 12—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated One Hour and Pulled at Temperatures Shown.

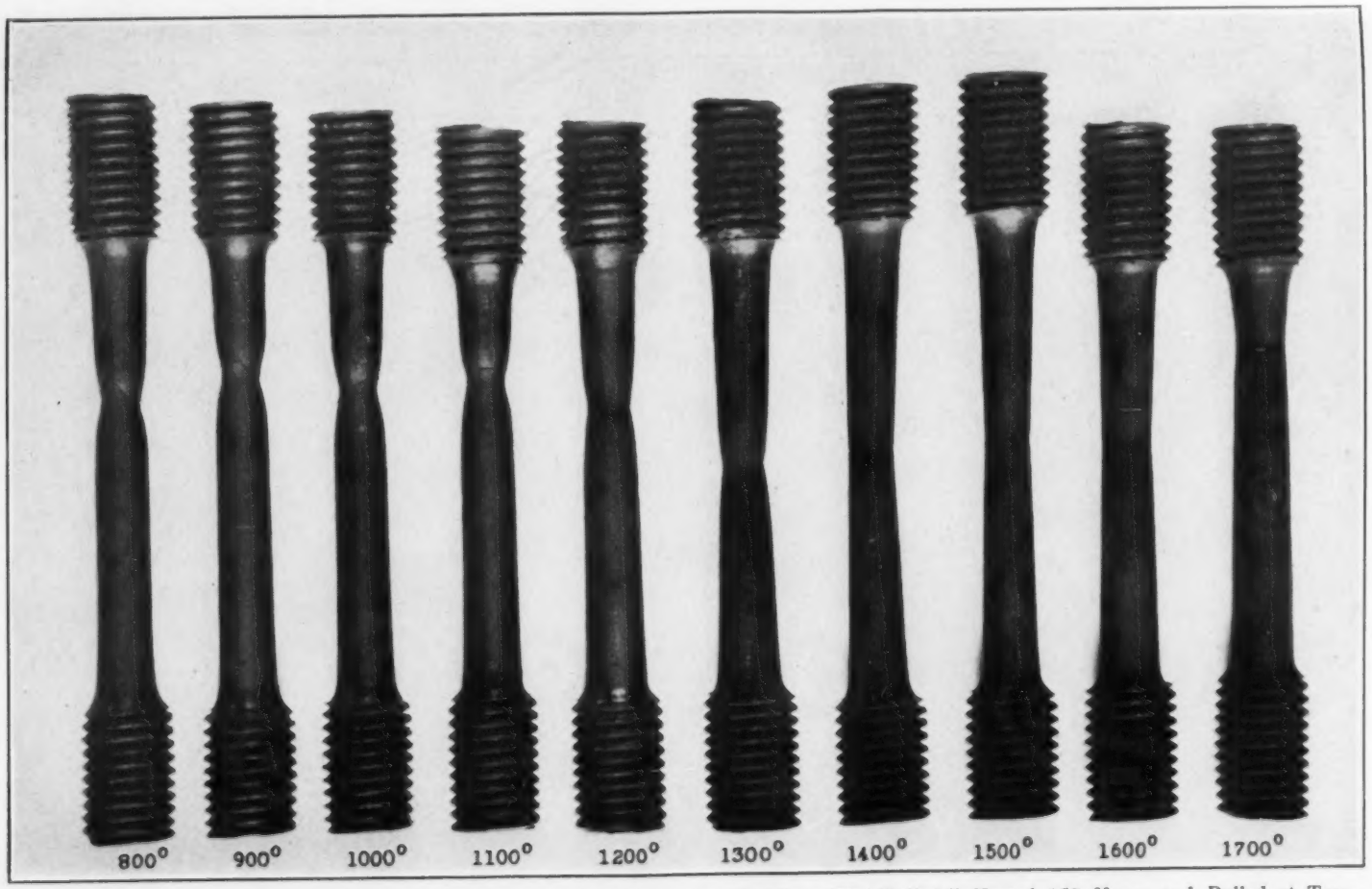


Plate 13—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, "Hot-Rolled," Heated 150 Hours and Pulled at Temperatures Shown.

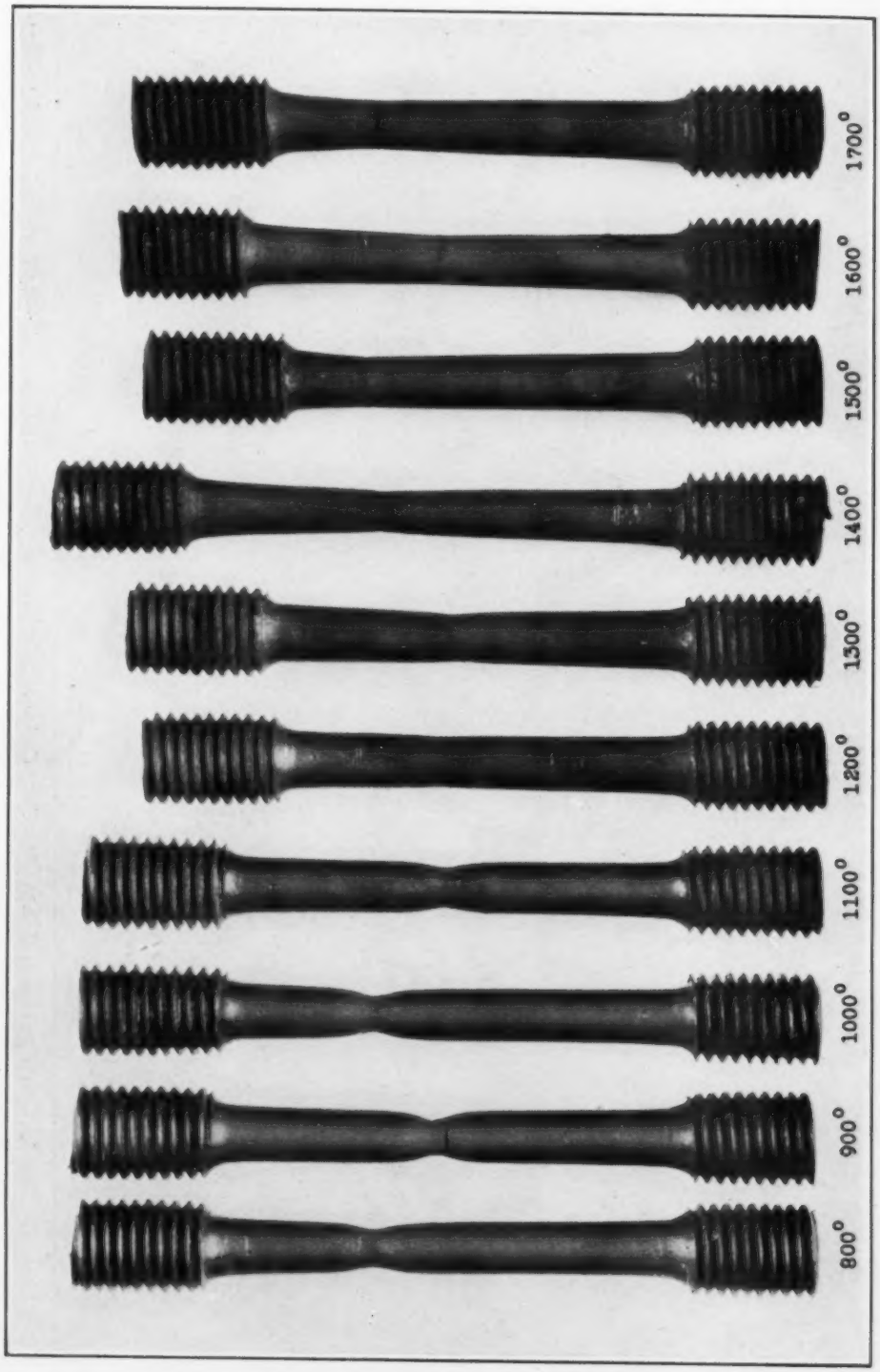


Plate 14—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

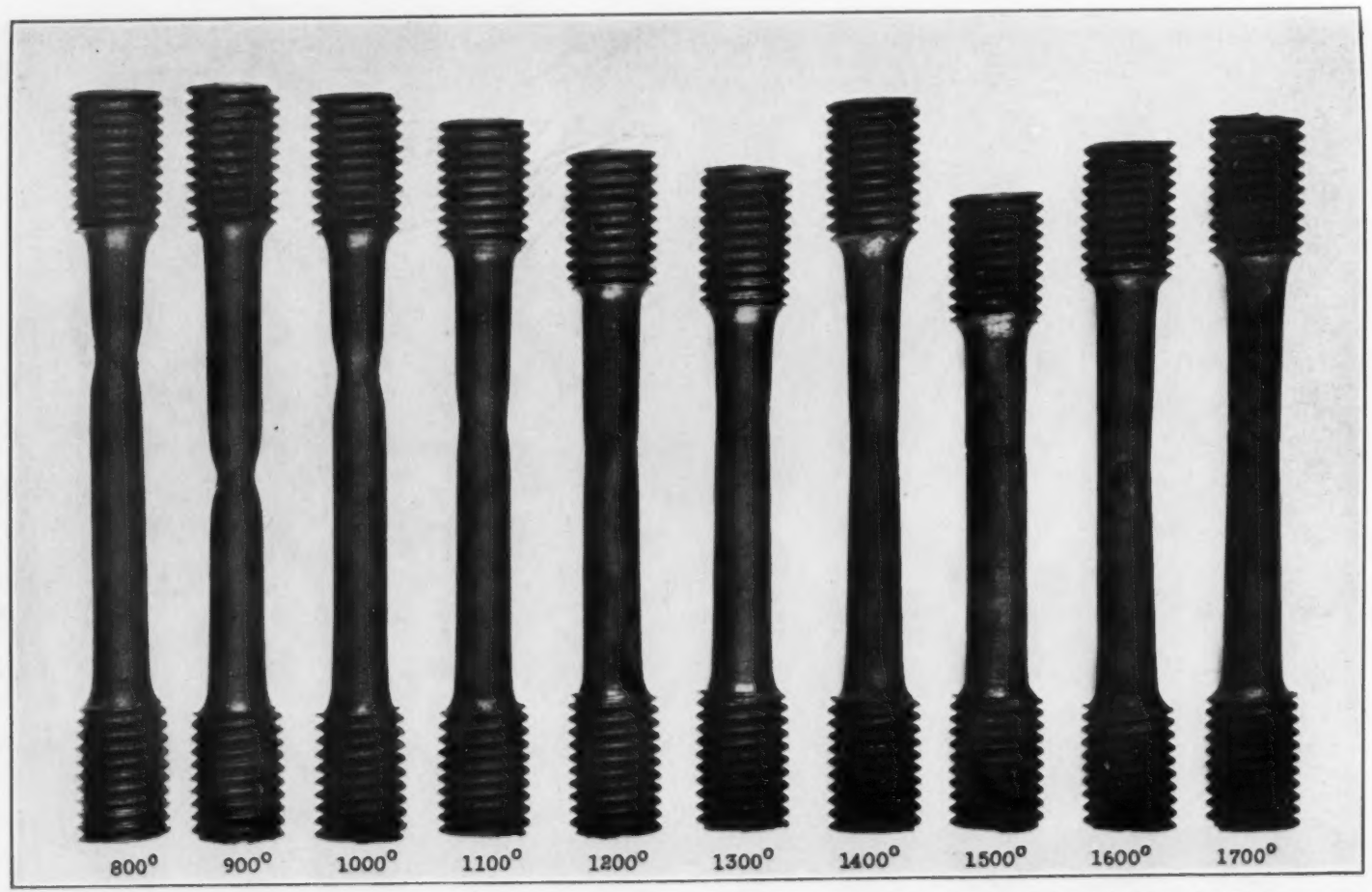


Plate 14—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 1900 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

Plate 15—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2100 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

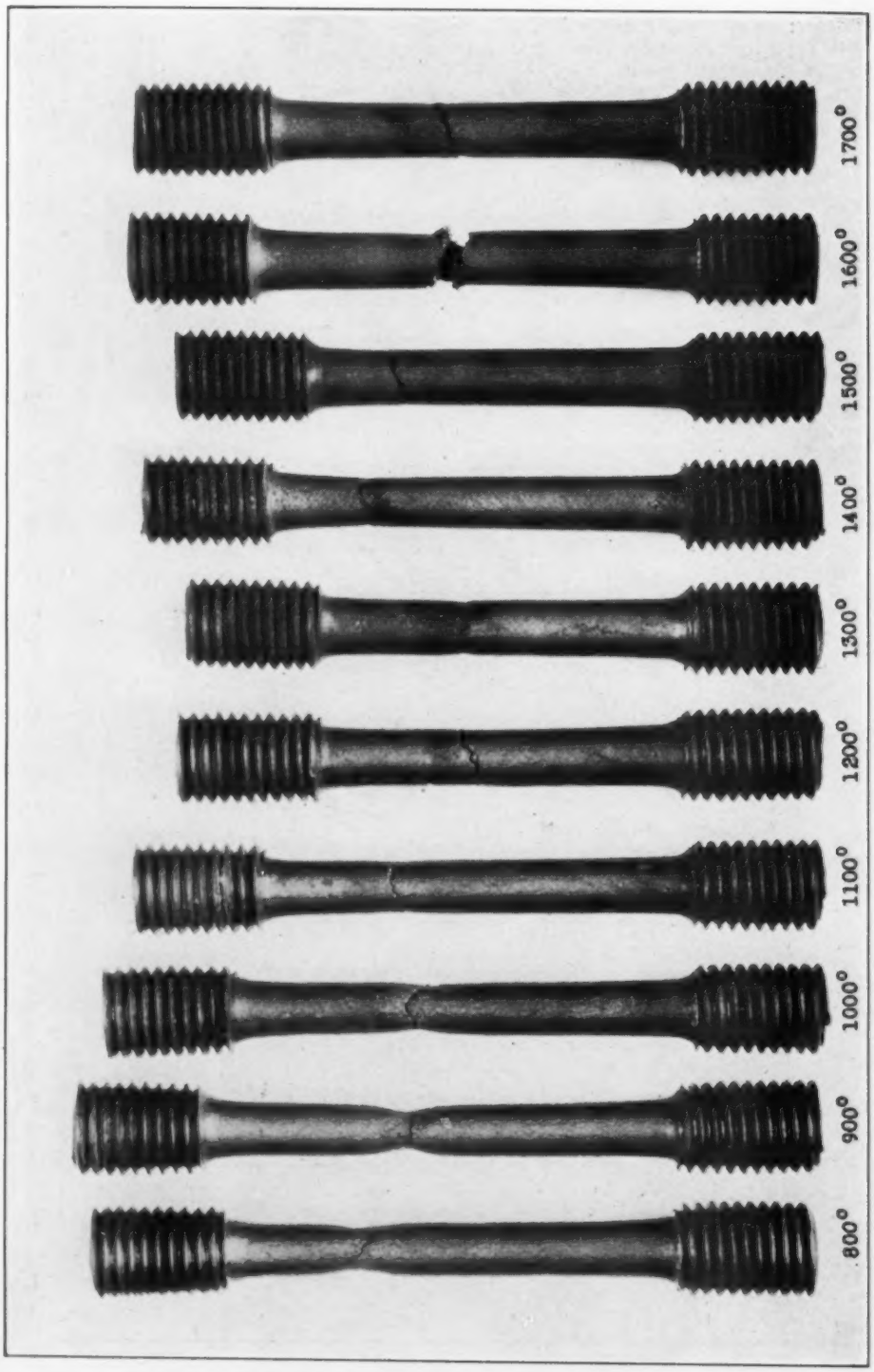


Plate 16—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

DISCUSSION

Written Discussion: By R. L. Duff, chief metallurgical engineer, Standard Oil Development Co., Elizabeth, N. J.

There is not much I can say in regard to Mr. Newell's paper on "Influences of Grain Size on the Properties and Corrosion Resistance of the 18-8 Iron-Chromium-Nickel Alloy for Elevated Temperature Service," other than that I am in perfect accord with Mr. Newell's complete article.

Written Discussion: By E. C. Wright, metallurgist, National Tube Company, Ellwood City, Pa.

We are pleased to note another paper from Mr. Newell on the 18-8 alloys, and appreciate the thorough manner in which he has described the effect of previous mill heat treatments on the properties of this metal for elevated temperature service and for resistance to corrosion. The whole question of the proper heat treatment of 18-8 alloys prior to introduction into service has been highly controversial, although the majority of manufacturers have insisted that quenching the material above 2000 degrees Fahr. (1095 degrees Cent.) [preferably 2100 degrees Fahr. (1150 degrees Cent.)] was most desirable.

In reviewing Mr. Newell's paper, we wish to point out some items which have influenced his results. In the first place the test pieces in Part II of the paper originated from hot-rolled ⅞ inch bar stock, although the photomicrographs exhibited for the hot-rolled material indicate that the hot rolling operation was probably completed at temperatures below the recrystallization temperature of about 1650 degrees Fahr. (900 degrees Cent.). Figs. 13A, 14A, 15A and 16A show quite clearly the effects of low finishing temperatures on the hot-rolled billets. It would, therefore, be expected that the short time high temperature tensile test on this material at temperatures below the recrystallization point might still exhibit the effects of the previous work, resulting in slightly higher tensile strength as reported in Tables II, III, IV, and V.

We also note that the annealing treatment imposed upon the hot-rolled specimens consisted of heating each lot for one hour at the selected temperatures prior to quenching. It is evident from the structures produced in heat treatment that the time of one hour at heat of different sizes of stock has resulted in considerable grain growth at all of the annealing temperatures; for example, in Fig. 13A and 13B the grain size in the hot-rolled specimen is estimated at 130 grains per square inch as compared to 11 grains per square inch in the sample heated to 1900 degrees Fahr. (1040 degrees Cent.). As the results of the short time tensile test and corrosion embrittlement test indicate that the metal quenched from 1900 degrees Fahr. (1040 degrees Cent.) is in most cases as good as the metal in the hot-rolled condition, it is believed that more careful regulation of the time at heat for the 1900 degrees Fahr. (1040 degrees Cent.) heat treatment to produce a finer grain structure would have been even more beneficial.

In attempting to regulate the grain size of commercial products, such as tubes or plates, made from 18-8 alloy, three contributing factors must be regulated to reach any required results. In manufacturing seamless tubes from this material the finishing temperature on the pipe mill varies quite widely depending upon the wall thickness and outside diameter of the material being rolled;

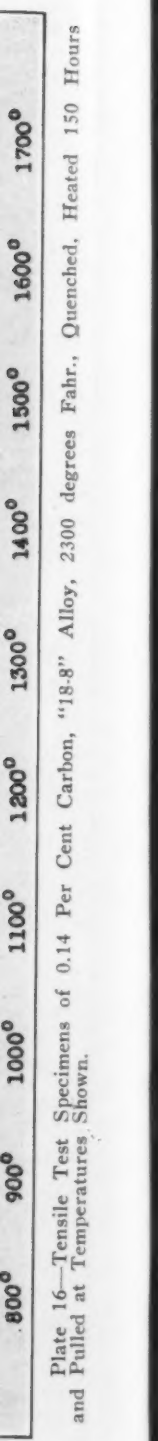


Plate 16—Tensile Test Specimens of 0.14 Per Cent Carbon, "18-8" Alloy, 2300 degrees Fahr., Quenched, Heated 150 Hours and Pulled at Temperatures Shown.

for example, a tube such as 2 inches outside diameter by ⅛ inch thick will be finished at a much lower temperature than a tube such as 5 inches outside diameter by ½ inch thick and the grain size in the two products will vary considerably. Following the production of the hot-rolled tube the grain size of the metal can be further controlled by adjustment of the annealing temperature between 1900 degrees Fahr. (1040 degrees Cent.) and 2100 degrees Fahr. (1150 degrees Cent.) and also the time at which the specimen is held at heat. This factor has long been recognized, and the time at annealing temperature in heat treating seamless tubes has varied between ten minutes at heat and forty-five minutes at heat, depending upon the wall thickness of the material being annealed. During the past four years we have produced several thousand tons of 18-8 tubing, none of which was ever heat treated above 1900 degrees Fahr. (1040 degrees Cent.), as the grain growth which always appears at higher temperatures was considered to be undesirable. The majority of the material has been used in cracking stills and as far as reported no instances of failure in any of these tubes have occurred.

Several important consumers of this alloy have also recognized the effect of grain size in their material and have either specified that the heat treatment be in a range of 1850 degrees Fahr. (1010 degrees Cent.) to 1950 degrees Fahr. (1066 degrees Cent.), or that the grain size of the finished product be maintained at some definite figure such as a minimum of twelve grains per square inch at one hundred diameters.

Written Discussion: By Albert Sauveur, Gordon McKay Professor of metallurgy and metallography, Harvard University, Cambridge, Mass.

What the author describes, in common with most writers, as "carbide precipitation" occurring in 18-8 steel at about 650 degrees Cent. (1200 degrees Fahr.) results, I believe, from the decomposition of the gamma solid solution through the formation of an alpha phase locating itself around the grain boundaries and along some crystallographic planes of the gamma solution. The alpha phase having little solubility for carbon, carbide particles are precipitated. It is probable that the austenitic condition of 18-8 steel is unstable at all temperatures below 650 degrees Cent. Lack of plasticity, however, prevents transformation from taking place until a temperature is reached sufficiently high to permit it. To prevent carbide precipitation, we should be able to delay the unstability of the chromium-nickel-carbon austenite until such temperature is reached when lack of plasticity will prevent decomposition. Having in mind solely the formation of the alpha phase and subsequent carbide precipitation, it seems evident that since grain boundaries invite precipitation, the less their extent the better. A steel consisting of a single grain should be free from grain boundary precipitation. I believe, however, that in such a grain the alpha phase would form along some of its crystallographic planes.

The influence of grain size so clearly and ably brought out by Mr. Newell is a distinct addition to our knowledge of the behavior of this important steel.

Written Discussion: By Prof. Dr. B. Strauss and Dr. P. Schafmeister, Fried. Krupp A. G., Essen, Germany. Translated by H. A. DeFries, Cleveland.

We congratulate Mr. Newell on his interesting paper on the influence of grain size on the properties and corrosion resistance of 18-8 iron-chromium-nickel alloy for elevated temperature service. Mr. Newell has made certain

facts available which, heretofore, were the private property of interested companies. On account of our experience and experiments, we are now presenting from our records our findings which, in most instances, are nothing else but a substantiation and amplification on the points brought forward so ably by Mr. Newell.

PART I. It is well known that steels which possess no transformation point or which attain no equilibrium even after prolonged heating (as, for instance 18-8) show grain growth with increasing temperatures. It is only possible to obtain fine grain on these steels by mechanical work. It is also known that the amount of working before heating, and also the duration of the heating cycle, are of great influence on the grain size insofar as deformation produces small grain size whereas prolonged heating produces grain growth. In amplification to the point set forth by Mr. Newell, we show in our Fig. 1 a recrystal-

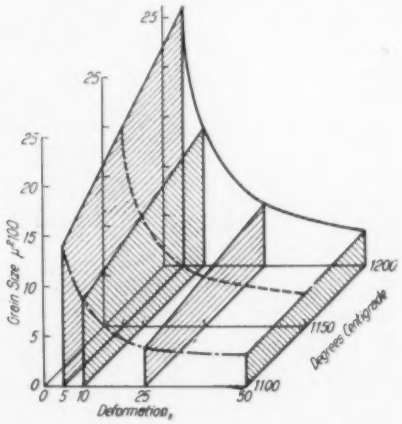


Fig. 1—Recrystallization Diagram of Austenitic (18-8) Chromium-Nickel Steel.

lization diagram for the 18-8 alloy, which is based on the investigations of H. Schottky and H. Jungbluth.[1] In practice we, therefore, have the following method to produce fine grained 18-8 materials—

1st. Comparatively heavy reductions at low temperatures
2nd. Short heating time in heat treating.

PART II. Before we commit ourselves to Mr. Newell's remarks regarding the effect of grain size on physical properties at elevated temperatures and on corrosion resistance after heating, we desire to discuss briefly the patented heat treatment[2] and the history of its development.

Austenitic chromium-nickel steels were produced in the beginning with higher carbon content, and were used as corrosion resistant materials at low temperatures. As maximum corrosion resistance is closely allied with a structure of maximum homogeneity, it was obvious that the alloys of higher carbon content were formerly quenched from a high temperature in order to obtain a

[1] *Stahl und Eisen*, Vol. 50, 1930, p. 1517.

[2] U. S. Patent No. 1404908 (31.1,22).

fully austenitic structure and the patented heat treatment was based on steels of such high carbon content. As an example for the beneficial influence of the higher quenching temperatures, we cite the loss in weight of chromium-nickel steels of the following analysis:

Sample	C	Ni	Cr
A	0.14 per cent	8.86 per cent	17.6 per cent
B	0.06 per cent	8.70 per cent	18.0 per cent

These samples were quenched in water from 970 and 1150 degrees Cent. and then tested in fuming nitric acid of a specific gravity of 1.52 at boiling temperature.

Table I

	Loss in weight in gr per hr. per m² surface (g/hm^2)	
Heat Treatment	A (0.14% C)	B (0.06% C)
970°/Water	5.16	3.20
1150°/Water	2.46	2.50

It is already known that the patented heat treatments produce an improvement in the physical properties at normal temperature in reference to elongation, reduction of area and deep drawing properties.

In order to prevent intercrystalline corrosion[3] large quantities of 18-8 alloys have lately been made with a carbon content of below 0.07 per cent. It is a natural consequence that alloys of such low carbon content become fully austenitic even when quenched from as low a temperature as approximately 1000 degrees Cent., but even in this case higher quenching temperatures are beneficial as to corrosion resistance in boiling, fuming nitric acid as is amply illustrated in Table I. Notwithstanding the fact that higher quenching temperatures produce grain growth on 18-8 material, we have means (as we have already stated) to prevent this grain growth, by selecting the working temperature, the degree of deformation and the duration of the heating cycle, and by proper selection we are then enabled to produce the grain size, which is fully satisfactory.

The next question asked would be—What were conditions under the circumstances as cited or as given by Mr. Newell regarding the use of the material under certain conditions wherein the operating temperatures of 400 to 900 degrees Cent. transformed the homogeneous austenitic structure into a non-homogeneous structure.

Tensile Properties. We can only substantiate the findings of Mr. Newell regarding tensile tests on 18-8 material, namely, that the elongation and reduction of area diminish with increasing quenching temperatures between approximately 600 to 900 degrees Cent. The following curves (Figs. 2 and 3) show our results with normal and low carbon 18-8 material; an explanation for the pronounced maxima at 500 degrees Cent. with 2 curves is unknown by us.

In our tests, samples which were previously quenched in water from 950

[3]U. S. Patent applied for.

and 1150 degrees Cent. were held for about 20 minutes at the testing temperture and then slowly pulled, using about 20 to 25 minutes. In comparison with the corresponding curves (Figs. 5 and 9) in Mr. Newell's article, it is evident that in our investigation the differences between the curves for the 2 quenching

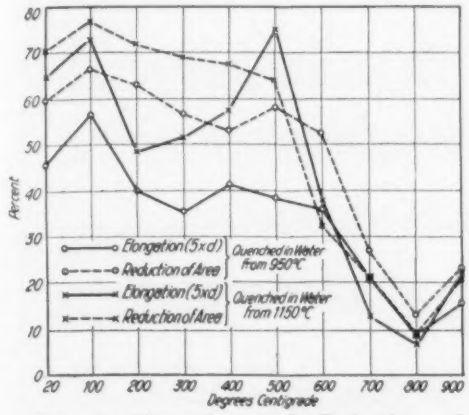


Fig. 2—Elongation and Reduction of Area on (18-8) Material at Different Temperatures; Time of Pull 20-25 Minutes. Analysis: Carbon 0.14, Nickel 8.78, Chromium 18.1.

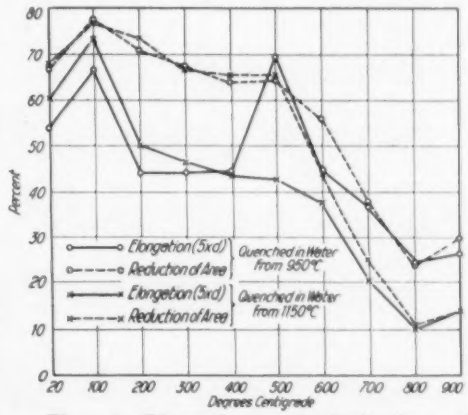


Fig. 3—Elongation and Reduction of Area on (18-8) Material at Different Temperatures; Time of Pull 20-25 Minutes. Analysis: Carbon 0.06, Nickel 9.22, Chromium 18.0.

temperatures is much less pronounced. We, therefore, wish to state (especially on account of the results as shown in Table II) that the speed at which the sample is pulled is of utmost importance. For tests which were made sometime ago, chromium-nickel steel quenched from 1150 degrees Cent. in water was used, and had the following analysis: carbon 0.22 per cent, nickel 6.85 per cent, and chromium 20.6 per cent.

Table II

Pulled at Degrees Cent.	Time of Pull	Elastic Limit Lbs./Sq. In.	Ultimate Strength Lbs./Sq. In.	Elongation %	Reduction of Area %
800	12 seconds	..	42,660	27	36
800	1 minute	15,640	28,440	16	24
800	10 minutes	..	19,900	5	11
800	42 minutes	..	21,330	4	8

The speed at which the samples were pulled by the tests made by Mr. Newell were from 2 to 15 min. and, therefore, could be of decided influence on the values obtained by him for elongation and reduction of area. What influence the grain size has upon the elongation and reduction of area at higher temperatures cannot be determined right off, totally aside from the fact that material of large grain size showed higher creep stress value.

In amplification of the values at high temperature of 18-8 material which has been heated for a long time, we give some values taken at room temperature and which were based on 18-8 materials which were heated for a long time. For this test 18-8 material of the following analysis was used:

Sample	C	Ni	Cr
A	0.12 per cent	9 per cent	18.1 per cent
B	0.06 per cent	9.22 per cent	18 per cent

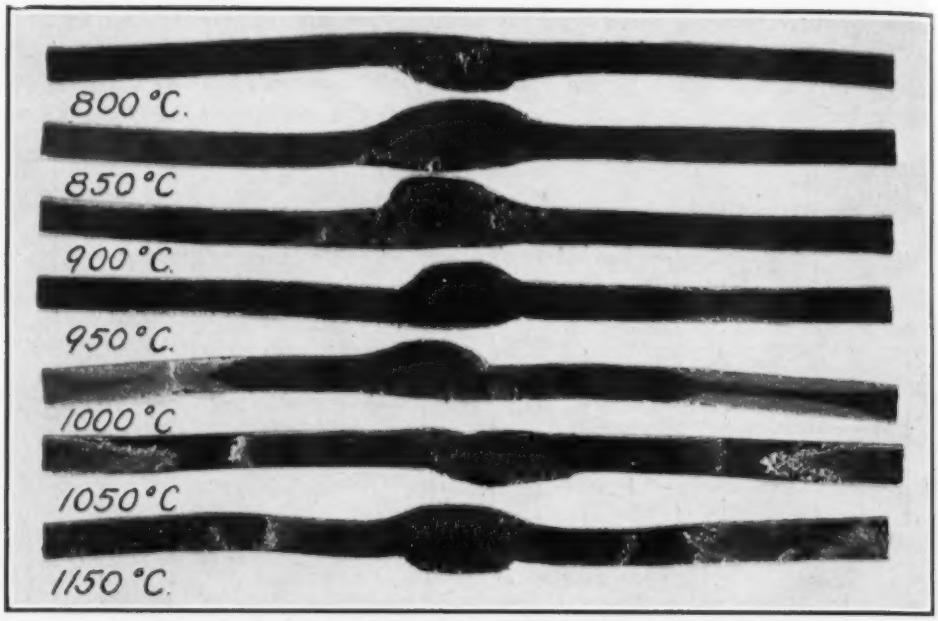


Fig. 4—Intercrystalline Corrosion of Acetylene-Welded (18-8) Sheets, 2 Millimeters Thick. Time of Boiling in Sulphuric Acid Copper Sulphate Solution—48 Hours. × 2. Before Welding Quenched from Temperatures Shown.

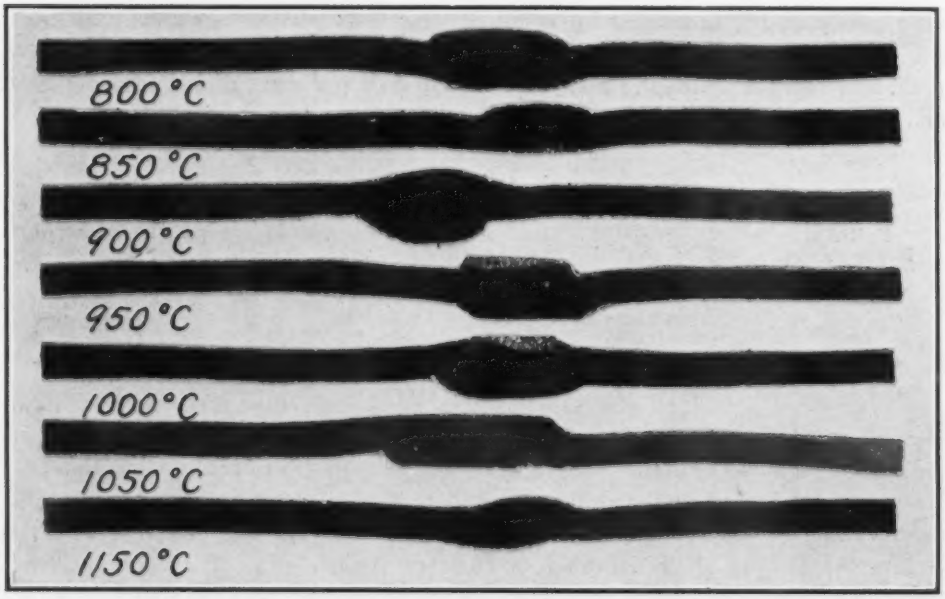


Fig. 5—Intercrystalline Corrosion of Acetylene-Welded (18-8) Sheets, 2 Millimeters Thick. Time of Boiling in Sulphuric Acid Copper Sulphate Solution—48 Hours. × 2. Before Welding Quenched from Temperatures Shown.

Table III

Steel	Treatment Degrees Cent.	Elastic Limit Lbs. per	Ultimate Strength Square Inch	Elongation (5D) %	Reduction of Area %	Impact † mkg/cm²
A	1150/water	42,240	92,450	60	68	21
(.12% C)	1150/300h 500 air	35,550	88,200	68	73	22
	1150/300h 600 air	44,000	93,850	57	65	21
	1150/300h 700 air	44,000	102,400	47	59	12
	1150/300h 800 air	34,100	98,100	50	60	4
B	1000/water	29,900	89,600	60	67	20
(.06% C)	1000/300h 500 air	32,700	88,200	61	69	16
	1000/300h 600 air	28,450	90,800	57	67	14
	1000/300h 700 air	25,600	89,600	53	66	13
	1000/300h 800 air	25,600	88,200	53	65	12

†Mesnager tests.

Even after heating at 700 to 800 degrees Cent. we observe no decrease in the elongation and in the reduction of area. Remarkable, however, is the decrease of the impact after long heating at 700 to 800 degrees Cent. 18-8 material at a low carbon content shows, however, much better under these conditions.

CORROSION-RESISTANCE. Our experience about the loss in general corrosion resistance on chemical attack (expressed in loss of weight) of the 18-8 by drawing it back between 400 and 900 degrees Cent., agrees with the results obtained by Mr. Newell. We were unable to obtain information that the quenching temperature has a deciding influence on the drawn 18-8 material when tested in boiling nitric acid. However, the duration of the annealing temperature and the carbon content are of greater influence. The corrosion attack is the heaviest with materials of high carbon content and when drawn between 600 and 700 degrees Cent. When the annealing has been carried on for a very long time, the corrosion attack generally becomes less.

In reference to the question of intercrystalline corrosion,[4] in this connection we have to observe the following points:

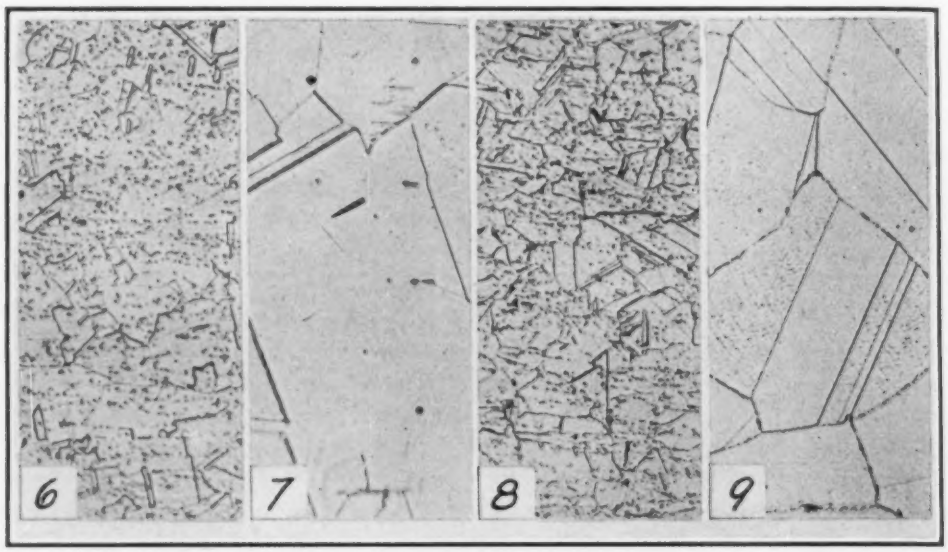
1. Influence of the carbon content
2. Influence of the drawing temperature
3. Influence of the quenching temperature
4. Influence of the drawing time.

Mr. H. D. Newell confirms our tests, namely, that the 18-8 material of low carbon content is immune against intercrystalline corrosion even after drawing at 500 to 900 degrees Cent. We furthermore found that the strongest intercrystalline corrosion appears in 18-8 material after a short time annealing at 600 to 700 degrees Cent. After drawing at 800-900 degrees Cent., the intercrystalline corrosion diminishes and at 500 degrees Cent. it appears only after heating for a very long time.

Our experiences regarding the influence of the quenching temperature in reference to the appearance of the intercrystalline corrosion are shown in Figs. 4 and 5. The samples which we used were quenched from various tempera-

[4]A complete illustration on the question of intercrystalline corrosion will appear in the very near future in an article gotten out by Dr. Schafmeister and Dr. Houdremont.

tures in water, were then welded by oxyacetylene and, therefore, the drawing time was very short. The welded samples were then boiled for about 48 hours in the usual sulphuric acid, copper sulphate solution (H_2SO_4 1:10 plus 10 per cent $CuSO_4$). It is, in substantiation of the results of Mr. Newell, easily seen that with 18-8 material of high carbon content with increasing quenching temperatures the intercrystalline corrosion increases. 18-8 material with low carbon content is immune against intercrystalline corrosion using a short annealing time after being quenched from almost any temperature. The deductions that Mr. Newell gives for this appearance, on account of the increase in



Figs. 6 to 9—Photomicrographs of 18-8 Steel.
Fig. 6—Water-quenched from 950 Degrees Cent.
Fig. 7—Water-quenched from 1150 Degrees Cent.
Fig. 8—Water-quenched from 950 Degrees Cent. Annealed 10 Hours at 600 Degrees Cent.
Fig. 9—Water-quenched from 1150 Degrees Cent. Annealed 10 Hours at 600 Degrees Cent.

grain size with increasing quenching temperature with subsequent carbide distribution, may be true in many instances, especially with hot-worked 18-8 material. We ask, however, to indicate here the manner of the carbide distribution and its influence of the intercrystalline corrosion. Figs. 6 and 7 show the structure of the 18-8 samples with 0.15 per cent carbon and which were quenched from 950-1150 degrees Cent. respectively, in water, previously shown in Figs. 4 and 5. The material which was quenched from 1150 degrees Cent. in water is homogeneous austenite with comparatively large grain, the sample quenched from 950 degrees Cent. in water on the contrary shows carbide precipitation in a fine-grained austenitic groundmass.

The latter structure always appears when the working of the 18-8 material has been carried on at the lowest possible temperature using a high degree of deformation and when the heat treating temperatures are below that temperature at which the carbide goes again in solution.[8]

[8]U. S. Patent applied for.

From the structure shown, we can derive the following explanation of the non-appearance of the intercrystalline corrosion at lower quenching temperatures. By water quenching from 1150 degrees Cent., the homogeneous austenite contains plenty of carbide in solution which precipitates by subsequent annealing at 600 to 700 degrees Cent. in the grain boundaries and appears in finely divided form which is especially dangerous and produces intercrystalline corrosion. The explanation for this is probably due to diminishing of the chromium content in the neighborhood of the grain boundaries.

In 18-8 materials which have been water-quenched from 950 degrees Cent. the austenite contains less carbide in solution, as free carbide is still present in the interior of the grains.

If the material is annealed afterwards:

(1). Less carbide precipitates

(2). The free carbides act as a crystallization nucleus to which the precipitated carbides migrate. In the grain boundaries themselves no finely divided carbide is present after an annealing of 600 to 700 degrees Cent. and therefore cannot cause intercrystalline corrosion. Figs. 8 and 9 give an explanation of the above theory and represent 18-8 material with about 0.15 per cent carbon which was heated for ten hours at 600 degrees Cent.

There remains only to mention the influence of the annealing time. In comparing Fig. 5 with the results obtained by Mr. Newell on 18-8 material with low carbon content, the important influence of the time is shown. While short time heating—for instance, welding—is not dangerous with this material, however, longer time of heating produces indications of intercrystalline destruction.

We only want to mention here briefly that by very long time heating at certain temperatures and with materials of corresponding carbon contents, 18-8 material can be produced in which the inclination towards intercrystalline corrosion is entirely absent.[6]

Written Discussion: By J. B. Romer, chief chemist, Babcock and Wilcox Tube Co., Bayonne, N. J.

The influence of grain size on the properties and corrosion resistance of the 18-8 iron-chromium-nickel alloy for elevated temperature service is a subject of great interest and Mr. Newell is to be congratulated on his excellent presentation of this subject.

It is interesting to know that he has determined that the small-grained hot-rolled and the material quenched from 1900 degrees Fahr. show better physical properties after fine carbides had been precipitated due to long time heating at 1200 degrees Fahr. than the larger-grained material after the same treatment.

The discussion of the relation of grain boundary area to the amount of carbides necessary to sufficiently deplete the grain boundary material of its chromium content brings out, in a clear manner, the effect of grain size. It is well illustrated, by his photomicrographs, that the attack is much more a surface effect on the fine-grained material.

In conducting some corrosion tests on an 18-8 alloy containing about 2.7

[6]D. R. patent applied for.

per cent silicon, we found that this alloy was more resistant to sulphuric acid corrosion when quenched from 2300 degrees Fahr. than when quenched from 1900 degrees Fahr., thus indicating that the higher temperature produces a more resistant material. It was further found that when the same material was heated for 150 hours at the carbide precipitating temperature of 1200 degrees Fahr. that the reverse was true, namely, that the large-grained material, which had been quenched from a high temperature, was less resistant to corrosion.

Since corrosion attacks the carbides precipitated at the grain boundaries, a prolonged corrosion test would tend to dissolve the carbides around the grain, thus causing a dislodging of the grain. The high temperature quench, producing large grains, is therefore detrimental when the material is to be used within the carbide-precipitating range of 1000 to 1400 degrees Fahr. This feature has been well brought out by Mr. Newell.

Written Discussion: By Victor N. Stefanides, Beaver Falls, Pa.

Mr. Newell having been associated with the chromium-nickel alloys for some time, has rather an intimate knowledge of them. It was, therefore, a real pleasure to read his excellent piece of work, for which he is to be congratulated.

The paper deals with generally accepted theories. So far much has been written and discussed about the intergranular carbide precipitation by such research workers as Strauss, Krivobok, Grossmann, Aborn, Bain and others. Due, however, to lack of any concrete evidence, it looks as though we are inclined to over-emphasize that hypothesis.

That there are some constituents separating at the grain boundaries, which in major part are carbides, we have sufficient evidence, but as to the depletion of chromium at the grain boundaries the evidence is still lacking.

A great deal of credit is due to Dr. Krivobok for propounding the theory of stresses set in into the grain boundaries induced by quenching in his very eminent work on "A Study on Constitution of High Manganese Steel," also to Prof. Sauveur and Mr. Chou, who have very ably shown, that alpha phase forms first at the boundaries and along the crystallographic planes of the austenite grains, in electric iron quenched from high temperature, in their work on "The Gamma-alpha Transformation in Pure Iron." That the phenomenon of carbide precipitation in 18-8 is similar to that of high manganese steel, and that the transformation from gamma to alpha is first taking place at the grain boundaries, as found in electrolytic iron by Prof. Sauveur, hardly need to be emphasized.

Ever since the theory of carbide precipitation with its accompanying impoverishment of chromium at the grain boundaries has been advanced, it has gained momentum, until now, when it is almost universal. The usual explanation for the carbide precipitation and its accompanying curse is, that the alloy is sluggish, which means in that language, that the carbide at a favorable temperature will readily precipitate, taking with it a certain amount of chromium from the matrix adjacent to the carbide, and the reparation ensuing is rather slow. Indeed, indications are that such relationship does exist. However, when we consider that the solubility of one element in another is a physico-chemical phenomenon, it soon becomes apparent, that we are dealing with somewhat different conditions.

Now, we know that solubility is defined as the property of one element

mixing with another in continuous proportion to form a homogeneous aggregate. From X-ray studies we know that solids are made up of atoms arranged in crystal lattices. We must, however, differentiate between two kinds of solid solutions, namely, those where the solute is a substitution element of solvent, and those in which the solute is an interstitial element. The substitution element will replace the solvent element and occupy its space, while the interstitial element will enter the solvent lattice and occupy the open spaces between the solvent atoms. It will suffice to say, that nickel and chromium are substitution elements, while the carbon is a well known interstitial element. At temperatures of 1200 degrees Fahr. the thermal agitation of atoms is indeed great when we consider that molten tin can dissolve platinum whose melting point is 3190 degrees Fahr. At any rate, it is conceivable that that temperature is sufficiently high to set the forces in action to repair any damage in equilibrium, especially with an element like chromium, which is soluble in iron in all proportions and does not form intermetallic compounds with it.

Carbon, as we know, is an interstitial element, and as such will occupy open spaces between the solvent atoms. The carbon being such, its solubility in iron is small which is even further reduced in 18-8, owing to nickel not forming carbides except on very rare occasions. The tendency of carbon in solution is two-fold, namely, that of occupying spaces in the solvent lattice, and that of forming compounds. The formation of compound will be chiefly determined by concentration, but the amount of solution in elementary form will depend upon temperature. As temperature is increased, more and more atoms of carbon will enter the space lattice until such time as the forces of combination are stronger and overcome the forces of diffusion. It is quite probable that the small elementary carbon atom will migrate with great freedom and velocity from one lattice to another, however, a compound may be too large to pass through the lattice, thus it becomes permanently attached in the lattice. Here, then, we have some indirect evidence that the carbon does not migrate to the grain boundaries as readily as it is generally supposed. Not only that, but as such becomes a stabilizer of austenite (face-centered space lattice), because the space lattices being crowded, the atomic arrangement cannot proceed to rearrange itself in such a way as to revert back to alpha (body-centered space lattice), until temperature drops and the solubility of carbon thus is decreased. In all probability, a carbon-free or very low carbon 18-8 alloy will retain its magnetic properties at all temperatures below melting. That such is the case, has been shown by Dr. Krivobok in his excellent work on "Further Studies on Chromium-Nickel-Iron and Related Alloys," however, he thinks that alloy of 0.01 per cent carbon, with which he was working, should have been nonmagnetic at temperatures 1600, 1800 and 1900 degrees Fahr., and not finding it so, he is of the opinion that some undetectable error crept in into his work.

Heating the alloy of 18-8, with a carbon compound, in some carbide precipitation range, the tendency becomes indeed great for the carbides to detach themselves from the space lattices, it becomes so great, that the grains are actually stressed, as is indicated by the innumerable twinning planes (Fig. 16), along which carbides are actually separating out. That, however, does not preclude the carbide separation in other parts of the grains, as is especially evident in

Fig. 16B. In the lower carbon alloy, Figs. 13 and 15, the gamma transformation is taking place very readily, more so than in the higher carbon alloy, which in the view of the above reasoning, would naturally follow. Magnetic measurements also seem to confirm this line of reasoning.

At the time the carbides are separating, they are then established entities, and the chemistry of the individual grains will not be disturbed. There will be, however, atomic disturbance, because the carbides having migrated from the open space lattices, left enough freedom for the atoms to rearrange themselves in such a way as to change the crystal lattice from gamma (face-centered space lattice) to alpha (body-centered space lattice). This phenomenon will be more noticeable and quicker the less the carbon. Of course, the same thing will happen by cold working the alloy, with the exception that the thermal agitation will be substituted by dynamic forces, the carbide precipitation being very minute. As soon as heat is applied, they will coalesce. This naturally leads us to the supposition that other elements may act as a stabilizer of austenite, and, indeed, such is the case, although when another stabilizer besides carbon is present, then the amount of soluble carbon should decrease.

In regard to corrosion due to precipitation of carbides and the accompanying depletion of chromium at the crystallographic planes, it can be said that as solution is a physico-chemical phenomenon, so is corrosion an electro-chemical phenomenon. That it is so, can readily be substantiated. Before doing so, however, an apology is due to Mr. Bain, for disagreeing with him. Mr. Bain, to prove that the corrosion was not an electro-chemical phenomenon, proceeded to roll solid gold particles into chromium rustless alloys to be sure to have insoluble cathodes. A very ingenious idea, indeed. This he subjected to some mild corrosion and did not observe any amount of deterioration in the vicinity of the cold cathode, concluding from that, that the corrosion is not an electrolytic one. Mr. Bain, however, overlooked that corrosion in an oxidizing acid forms a protective coating consisting of chromium oxides, which not only protects the metal from further corrosion, but acts as an insulator to electric current. The current not being of a high density, the film may be sufficiently thick so that the current cannot puncture it, thus arresting any further corrosion. In a nonoxidizing acid, where the film formation does not take place, the case would be different.

The writer has seen an ⅛ inch thick Toncan iron sheet, which has been brazed. The sheet has been immersed in Pittsburgh tap water and resisted corrosion for two years, and in subsequent three months, very badly corroded in the vicinity of the brazed section. For the sake of brevity, we will not go into a discussion of what was taking place, but it will suffice to say, that electrolytic action does not necessarily take place immediately, but under some conditions it may take time to build up the necessary amount of current density.

Since 1926 the writer has investigated almost every corrosion resisting alloy. Due to this investigation and study, he became thoroughly convinced that corrosion is simply electro-chemical phenomena. The study of corrosion was primarily confined to hydrogen generating acids. To substantiate further that the corrosion is an electro-chemical phenomenon, the writer conducted the following experiment.

An austenitic (not the high nickel) alloy was selected, whose corrosion

rate in 10 per cent sulphuric acid at boiling temperature, was 0.00015 or less grams per square inch per hour. This alloy was subjected to 10 per cent boiling sulphuric acid for two weeks. (It was necessary to boil it that long on account of the slow rate of corrosion.) The alloy retained its bright surface for quite a long time, but eventually started to discolor, forming at the start a dark brown and eventually a black film. At the end of two weeks, the samples were taken out and washed, after which they were immersed in mild boiling hydrochloric acid. The boiling hydrochloric acid removed the film by attacking the alloy under the film. The film thus removed was washed and analyzed. The analysis showed it to be an oxide. Precautions were taken to remove the oxygen from the solutions before immersing the samples. Here we have an oxide film in a hydrogen generating acid. Where did it come from? Before going further into this discussion, perhaps, it will be of some interest to point out how the writer came to think that the discolored film was oxide.

On previous occasions it was observed, that when samples of this alloy were subjected to boiling sulphuric acid corrosion, at times there would be a small area from which gas would be evolved. At the path of the evolution of this gas, there would be a dark streak forming after which the evolution of the gas diminished and gradually stopped entirely. From this observation it was reasoned that the gas could not have been hydrogen because it would not discolor the metal where it came in contact with it. The only alternative was oxygen, which was proven to be such by the above experiment. Now, from electro-chemistry we know that sulphuric acid will break up to positive hydrogen and negative SO_4 radical. This is a well known phenomenon, and as such we shall pass with the remark, that the SO_4 radical may directly combine with the ions from the anode, or may break up H_2O liberating oxygen as the case may be, depending upon the solubility of the anode. However, here is the source of the oxygen.

As resistant as this alloy is to sulphuric acid corrosion, it is quite possible to bring about intergranular deterioration similar to that of 18-8, providing we permit the carbides to precipitate. This has been observed by the writer. The Durimets are also subject to the intercrystalline deterioration even with as high as 35 per cent nickel. Yet, strange as it may seem, the early Durimets, without any chromium, are nearly as much susceptible to the intercrystalline corrosion as those with chromium. Why then do we have a greater corrosion in presence of chromium and a lesser in the absence of it? Because the potential difference between carbides and the matrix is increased by the presence of chromium. Do we not know that the chromium-iron alloys have greater solubility in sulphuric acid than pure iron? Indeed, we do. The writer has made two austenitic alloys, one containing 8.36 per cent chromium, the other 19.86 per cent chromium. The carbon analyzed 0.20 per cent in both, and the other elements present were very close. We have then an alloy here identical in every respect, except the chromium content. Samples of the two alloys were heated at 2000, 2100, 2200 and 2300 degrees Fahr. for half an hour and quenched from that temperature in cold water. The samples were then machined and subjected to sulphuric acid (10 per cent) corrosion at boiling temperature for 25 hours. The results given below are tabulated in grams per square inch per hour.

	2000 Degrees Fahr.	2100 Degrees Fahr.	2200 Degrees Fahr.	2300 Degrees Fahr.
High chromium	0.01036	0.00086	0.00055	0.00647
Low chromium	0.00007	0.00009	0.00296	0.00014

Without going into any further discussion of these results, it will suffice to point out the greater solubility of the high chromium alloy. Does that not follow from the above, that if we have depletion of chromium at the grain boundaries, then the solubility due to such a condition should decrease? In all probability it does. Corrosion then is simply an electrochemical phenomenon, depending directly upon potential difference between carbides and matrix, the size of the carbides being in direct proportion with current density. Indirectly, the stresses at the grain boundaries and the metastable condition in the alloy will also have a great effect upon electrolytic action.

Written Discussion: By Robert H. Aborn, United States Steel Corporation Research Laboratory, Kearny, N. J.

This paper carries out a well-conceived program in an admirable manner, and the conclusions, logically derived as they are from abundant data, warrant the attention of all who are concerned with this type of stainless steel.

With regard to Fig. 17, it would be interesting to know what effect, if any, Mr. Newell considers that the quenching temperature (and time) would have on the location and magnitude of the maximum corrosion rate.

In these alloys it seems unwise to say that the discontinuities in the strength curves are due to transformations, principally because the inordinate sluggishness of the alloys generally results in a transformation occurring over a wide range of temperature. At any rate the true A_1 transformation on heating results in lessening rather than increasing the amount of ferrite. Furthermore, it does not seem likely, in view of other well-confirmed observations on such alloys, that the A_3 transformation could be found as high as 1600 degrees Fahr. particularly after 150 hours at temperature. Magnetic and X-ray observations on the fractured test specimens should throw much light on these points.

The conclusion drawn by the author that the optimum treatment for low temperature service is not the optimum for temperatures within the carbide precipitation range provides an excellent illustration of a principle being rather slowly recognized in the application of stainless steels. The best treatment for one use is by no means the best for other uses.

Oral Discussion

A. V. DeForest:[7] I wish first to compliment Mr. Newell on this thorough and careful paper. It represents an enormous amount of careful labor.

In regard to the mechanical behavior of 18-8 under conditions of stress and temperature, the grain size variable is very important, as Mr. Newell has well proved, but there is another variable which I would like to introduce into this already complicated system. The intergranular attack, so disastrous in still tubes, is a function of stress as well as composition of the steel and precipitation at grain boundaries. A test for the stability of the metal should include stress, for corroding agents which have no effect in the unloaded state may

[7]Research metallurgist, American Chain Company, Bridgeport, Conn.

attack grain boundaries under service loads, and reduce the available elongation to nothing. Under these conditions we have spontaneous disintegration as in the season cracking of brass. This dangerous possibility is not shown by the ordinary corrosion or creep tests, unless the latter are carried out simultaneously.

F. R. PALMER:[8] In reading both Mr. Newell's and Dr. Krivobok's paper I noticed in their photomicrographs that Murakami's reagent was used to develop the grain boundaries. I would like to ask whether they proved that the reagent used really does develop chromium carbide? My recollection is that this alkaline ferri-cyanide solution does not attack chromium carbide—even when applied hot. The reagent was used hot and cold to identify the double iron-chromium carbides and did not attack the simple chromium carbide. If Murakami's solution does not attack Cr_4C but does attack the intermediate double carbides, perhaps that fact may give us a valuable clue as to what is really happening in these grain boundaries.

I like Mr. DeForest's suggestion of strain. It has run in my mind for a long time that, with two phases of different specific volume present and compressed one within the other, the resulting strain may be part of the answer. There are other facts that point toward the strain theory and away from the carbide deposition theory. If we take a 0.30 per cent carbon, 20.00 per cent chromium steel (which is ferritic and contains no gamma iron so far as we know) and submit it to the acid copper sulphate solution, we get no attack. If we take the same steel and quench it from 2300 degrees Fahr., we get a mixed structure of austenite and chromium-ferrite (or martensite) and with these two phases together we do get copper sulphate disintegration. In this case, we have no nickel present nor can it be a question of carbide deposition because the treatment by which we make our steel susceptible to the attack is one which dissolves the carbide. Thus in a simple chromium iron, the presence of austenite and ferrite together will induce attack very similar to the chromium-nickels but if we have the ferrite alone we do not get it. We also know in our chromium-nickel steels that when we have only the gamma phase we do not get it, but when we get the alpha and gamma together we do get it. This observation regarding the behavior of simple chromium irons may be of value to those who are doing so much work on the chromium-nickel alloys.

DR. J. A. MATHEWS:[9] Mr. Palmer's remarks are the first I have heard mentioning the application of the copper sulphate solution to plain chromium iron. I was just about to suggest that we had found the same effect as Mr. Palmer mentioned. In that steel we are not dealing with the austenite phase present in great quantity, even when quenched from 2300 degrees Fahr. as suggested.

Now, the microstructure will show that there are carbides present in the plain chromium iron after low temperature treatment at 1000 or 1100 degrees Fahr.

Suppose that those carbides have come out of a solid solution and that

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[8]Assistant to the president, The Carpenter Steel Company, Reading, Pa.

[9]Vice-president, Crucible Steel Company of America, New York City.

there has been chromium impoverishment. We still must have left 22 or 23 per cent chromium in solid solution, and it would hardly seem that ferrite containing 23 per cent of chromium was particularly subject to chemical attack. In the presence of all these people who have been studying this subject so diligently, I would like to suggest a doubt whether we have as yet explained the cause of the intergranular attack, I mean the embrittlement attack, when we say "impoverishment" or "carbide precipitation," or both. I am under the impression that the carbides on the grain boundaries which are colored, as shown in the picture, are not so much affected in the attack. I think it is more that shaded boundary—possibly you might call it a troostite—rather than the actual carbides which you can see are responsible for embrittlement.

Author's Closure

The author is pleased to note that Mr. R. L. Duff is in accord with the subject matter of the paper. He represents a company that is one of the largest users of the alloy for elevated temperature service.

Professor Sauveur points to the decomposition of the gamma solid solution with formation of the alpha phase at grain boundaries and crystallographic planes. The precipitation of carbides is then permitted at these points because of the lowered solubility of carbon in this phase. It is probable that this occurs in the ordinary 18-8 alloy because of its nearness to boundary composition in the austenite field. On the other hand, the same phenomena of carbide precipitation and intergranular embrittlement seems to hold in alloys containing substantially more nickel. In such cases, carbide precipitation results at grain boundaries and elsewhere without decomposition of the gamma solution as measured by magnetic susceptibility tests. This would point to decreased solubility of carbon in the undecomposed gamma phase which permits sufficient carbide precipitation to do harm at certain temperatures. A method to delay unstability of the chromium-nickel-carbon austenite or to increase carbon solubility in the gamma phase at the lower temperatures would be welcomed. In the meantime our best defense is to reduce the carbon content of the alloy to a minimum.

While grain boundaries do invite precipitation, they do not control decomposition nor subsequent carbide precipitation, consequently, the greater their extent, the more favorable will be the distribution of the precipitated carbides which must precipitate in any event. That is to say, for any given composition, the decomposition and precipitation under equilibrium conditions will be the same in amount regardless of grain size. Dr. Sauveur's discussion was welcomed and suggests the interesting study of decomposition in extremely large grained alloys.

Concerning Mr. Wright's discussion, the heat treatments given the test pieces in Part II of the paper were not commercial treatments in any sense but were purely to induce certain differences in grain size which might be studied. The finishing temperature of the hot-rolled bar stock was not known, but it could not have been much below the recrystallization temperature, otherwise strain markings would have occurred within the grains and elongated grains would have been evident in longitudinal sections.

Many manufacturers have insisted on quenching the material from above 2000 degrees Fahr. and, while this is desirable for many low temperature applications, it is not considered desirable by the author for applications where the alloy is to operate within the carbide precipitation range. The higher short time tensile values for the hot-rolled materials are not important in the light of recent creep investigations. While the 1900 degrees Fahr., quenched material is not as satisfactory as the hot-rolled alloy, it is agreed that regulation of the time at heat at this temperature would produce a finer and more beneficial structure.

It is believed that regulation of grain size of commercial products such as tubes or plate of 18-8 alloys intended for elevated temperature service, will result in a more reliable alloy. This is being done in our own mill at the present time and, although the grain size is not altogether uniform, it does not matter so much as long as the average size is below a certain value. It is gratifying that several important consumers have recognized the value of small-grained material and have so indicated by specifying heat treatment or a maximum grain count. This is largely due to work instigated by the author and called to the attention of consumers.

The author was pleased to receive Mr. Romer's comments, and his experiments showing the silicon containing alloy to be similarly affected, are extremely interesting. From some additional experiments recently conducted, it is believed that ductility at elevated temperature and corrosion-resistance after heating of many of the austenitic stainless compositions, are influenced by grain size in precisely the same manner as ordinary 18-8.

Discussion by Dr. Strauss, the inventor of this interesting and useful steel alloy and by his co-worker, Dr. P. Schafmeister, is indeed gratifying to the author. Their discussion is a distinct addition to the paper. It is also most pleasing to find their experiences and experiments a substantiation of the conclusions arrived at in my paper.

Although my data were purely to call attention to the comparative properties and corrosion-resistance of large and small-grained alloy, it is agreed that the production of fine grain may be accomplished by comparatively heavy reductions at low temperatures and by short heating time in heat treating after working. In this connection, the heat treating temperatures must be carefully controlled to produce the desired result. The grain size, on recrystallization of the alloy, is affected by strain, time and temperature.

In the introduction of the paper it was pointed out that maximum benefit to certain properties was secured by heat treating according to the original patented heat treatment and for low temperature applications, maximum corrosion-resistance and greatest ductility in the cold are thus secured.

It is interesting that Dr. Strauss has recognized the value of fine-grained alloy for elevated temperature service and has evolved a procedure and applied for a patent in which the working temperature, degree of deformation and duration of heating cycle are controlled so as to produce a satisfactory grain size.

The results of Drs. Strauss and Schafmeister's tests shown in Figs. 2 and 3 closely parallel my tests although the differences shown by them are not so great as between fine and coarse-grained alloys. The speed at which the sample is pulled is of importance but was constant in my tests at 0.08 inch

per minute in every specimen pulled. The time, 2 to 15 minutes for rupture to occur, therefore, depended entirely on the ductility of the specimen as affected by grain size. The distance the cross heads of the testing machine traveled before the specimen broke was governed by the individual ductility of the specimen as the pulling speed was not altered throughout the tests.

The data shown in Table III of their discussion is interesting and points out that long heating does not seriously affect properties of the metals at room temperature. The impact value of the higher carbon alloy is reduced to a greater extent than the lower carbon, particularly at 800 degrees Cent. (1470 degrees Fahr.). The explanation given for the nonappearance of intercrystalline corrosion at the lower quenching temperatures may explain in part, the resistance of the low carbon alloy to this form of attack. The precipitation of carbides at 1600 or 1700 degrees Fahr., followed by reparation of boundary by diffusion at these temperatures, results in greater resistance to intercrystalline attack. Again the remaining carbon in solution at such temperatures may not be sufficient to cause damage at the lower temperatures, particularly if sufficient boundary extent is available. The micrographs shown in their Figs. 6 and 8 are of relatively high carbon content alloy and may not depict the condition that would obtain with low carbon material.

Discussion by one so well informed on iron-nickel-chromium alloys as Dr. Aborn is indeed welcomed. Concerning the effect of time and quenching temperature on the location and magnitude of the maximum corrosion rate shown in Fig. 17, it is believed that the magnitude would be affected to a greater extent than the location. While a comparative study has been made of several different alloys, the effect of heat treatment on corrosion rate after tempering has not been studied to any great extent because of the difficulty of ascertaining true loss in weight after intergranular corrosion has taken place. In this connection, the corrosion rate of the alloy is of lesser importance than its ability to resist intergranular attack.

The discontinuities in the strength curves, especially in the low carbon alloy, were so pronounced that it is logical to ascribe them to transformations. Lester[10] found a well defined transformation point on both heating and cooling in 0.09 per cent carbon 18-8 alloy. On heating, this temperature was 1330 degrees Fahr. (720 degrees Cent.) which closely checks the temperatures found by the author on testing the 0.05 per cent carbon alloy after heating one hour. While it is agreed that the sluggishness of the alloy might result in transformation occurring over a wide range of temperatures, the sluggishness would be greatly reduced by the combined effect of long heating and mechanical work during pulling of the specimens at elevated temperature. This would result in an approach to equilibrium and possibly a maximum amount of ferrite. This is also accompanied by ferrite formation due to carbide precipitation making the effect additive. The partial solution of the ferrite formed by long heating and mechanical work could then be interpreted as marking the A_1 point and produce such alteration in structure as to provide maintained strength at the temperatures shown in Fig. 4. The increase in strength between 1500

[10]H. H. Lester, "The Brittle Range in 18 and 8 Chromium-Nickel-Iron," TRANSACTIONS, American Society for Steel Treating, Vol. 16, Nov. 1929, p. 743.

and 1600 degrees Fahr. could then mark the temperature at which total transformation of austenite occurs. It is somewhat difficult to visualize these transformations in such light because of the sluggishness of the alloy and the changes in composition induced by carbide precipitation. As suggested by Dr. Aborn, magnetic and X-ray observations on the fractured test specimens should throw much light on these points.

The theories on intergranular corrosion presented in Mr. Stefanides' discussion are most interesting. Grain boundary strain or electrolytic corrosion may be in part the answer to the phenomena of disintegration of these alloys. The writer has endeavored in his paper to point out the susceptibility of such attack as influenced by grain size rather than describe the mechanism by which the alloys fail. In industrial applications, reduction of susceptibility to intergranular failure is an important step.

The term "Strauss Embrittlement Test" has been used in the paper to describe the copper sulphate-sulphuric acid corrosion test employed after tempering the 18-8 alloy. In justice to Dr. W. H. Hatfield, whom I recently visited in Sheffield, I learned that this test was a development of the Brown-Firth Laboratories and was subsequently called to Doctor Strauss' attention. Doctor Strauss later adopted it as a means of studying weld decay.

I was pleased to have the comments of Mr. DeForest concerning stress, and I hope at some time stress-corrosion tests will be made on these alloys.

I was pleased also to have the comments of Mr. Palmer. They were very interesting and point to some work that could be done to identify the carbides that could come down.

Replying to Dr. Mathews, most of the failures of the intergranular type have been in the 18-8 alloy and not in the straight chromium alloy.

In conclusion, I wish to thank all those who have taken part in the interesting discussions of my paper.

INSPECTION OF WELDS WITH GAMMA RAYS

By Gilbert E. Doan

Abstract

The gamma-ray method gives adequate results for the inspection of welds, according to tests made by the author at Lehigh University. Tests on good welds and bad welds revealed each kind without fail. Not only were the defects plainly visible in the bad welds, but the good welds were revealed as sound, in each case. The welds were fusion welds made in ½-inch and ⅝-inch steel plate, by five different commercial firms, and submitted for test. The tests were carried out by two undergraduate students.

THE penetrative power of gamma rays has been shown[1] adequate for inspecting steel castings as thick as 10 inches. The sensitivity of the method reveals flaws as slight as 2 per cent of the total thickness of the object examined. These limits of penetration and sensitivity would seem to indicate the method as entirely suitable for inspecting welds. Certainly, the penetration is adequate, for few welds are made in members above 6 inches in thickness.

But there might be some doubt whether the particular types of flaws which may occur in welds would be revealed by this method of inspection. For instance, shrinkage cracks, cold laps or lack of fusion, porosity and slag inclusions are among the faults found in welding that is improperly or carelessly done. Will the gamma-ray method reveal these flaws? How clearly will they be observed? Are any particular precautions necessary for such inspection? These are the questions which naturally arise.

It would create an erroneous impression to indicate here that final perfection of the gamma-ray method for inspecting welds had been achieved, for such is not the case. There will no doubt be many refinements and improvements in this field in the years to

[1]Mehl, Doan and Barrett, Transactions, American Society for Steel Treating, Vol. 18, 1930, p. 1192.

A paper presented before the Thirteenth Annual Convention of the society held in Boston, September 21 to 25, 1931. The author, Gilbert E. Doan, is a member of the society and is Associate Professor of Physical Metallurgy, Lehigh University, Bethlehem, Pa. Manuscript received June 20, 1931.

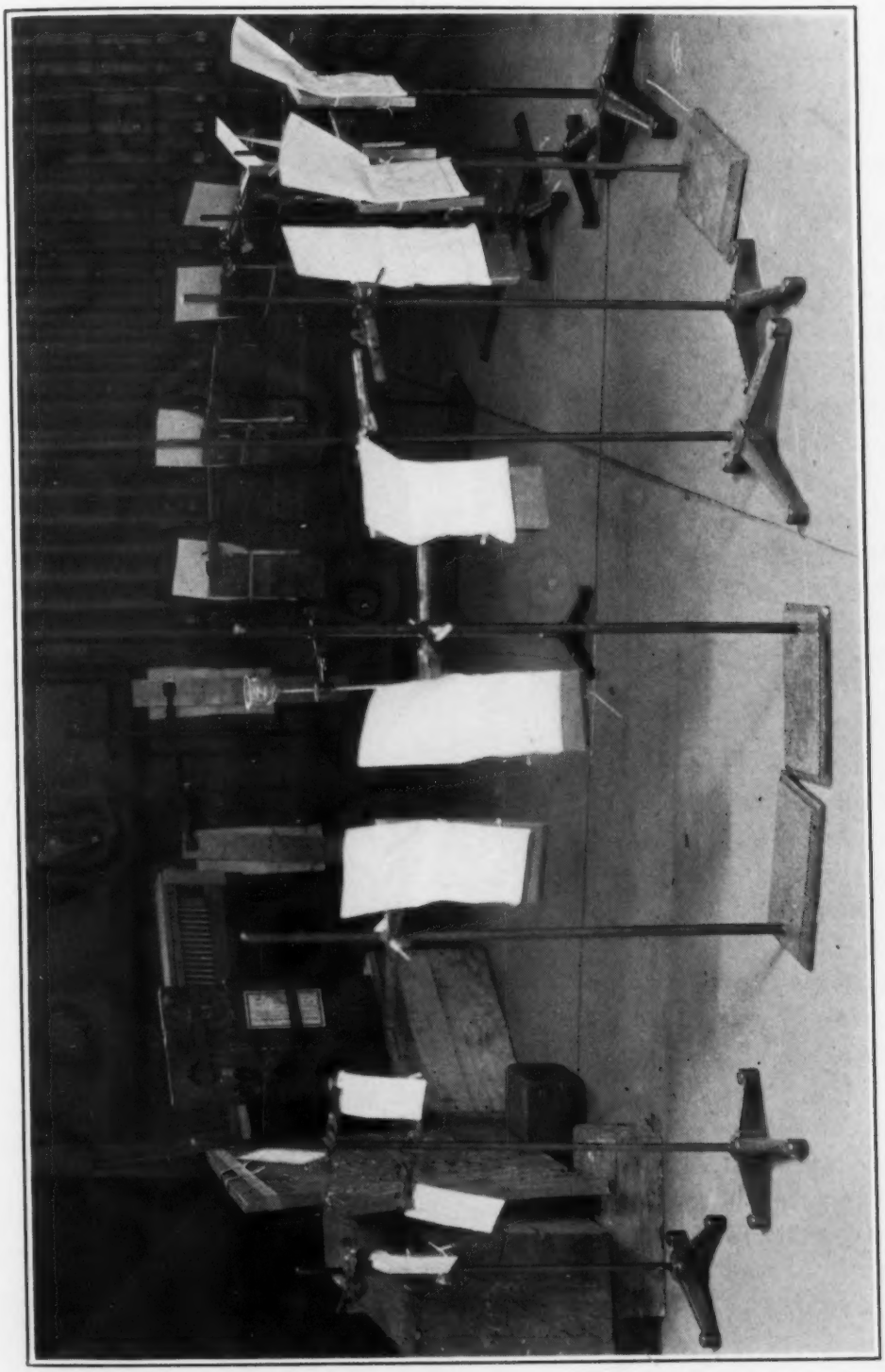

Fig. 1—Showing Method of Setting Up Welded Specimens to be Gamma-Rayed.

come. The purpose of this description is merely to show how well the method in its present state is suited to the examination of welds, where desired. The experiments were carried out at Lehigh University at the time of the Annual Welding Symposium, and the results were exhibited to the guests present.

Two welds each were submitted by five commercial companies, one very good weld and one as bad as it was possible to make it, from each company. The thickness of the welds proper ranged from 0.60 up to 1.00 inches. All welds were of the electric arc type. The radium was a very small capsule (1/20 gram) lent for the purpose by the Radon Co. Because of the very small quantity of radium used, the exposure time was unusually long, as will be seen below. Eastman duplitized X-ray film was used in duplicate, and in contact with lead foil. The usual methods of developing and fixing for such films were followed. The weld specimens were supported as shown in Fig. 1, the thinner welds being placed farther from the radio-active source, so that the exposure time would be the same for all specimens. The distances were from 31 to 36 inches. Twenty weld specimens prepared for tension test were exposed at the same time, as appears in the picture also.

The exposure time was about 18 hours with 1/20 gram of radium in accordance with the graphs of Barrett, Gezelius and Mehl.[2] With one gram it would be reduced to less than one hour. While some 30 specimens were exposed at this time it is obvious that less than $\frac{1}{10}$ of the space around the radium was used. With proper mounting, several hundred specimens could be exposed at one time. Thus the time of exposure per specimen, with a one gram source, would be in the neighborhood of 10 seconds. Extremely short exposure time is, however, in general of no great advantage.

The preparation of the films, as well as their exposure and development, was carried out by two undergraduate students, J. R. Hewitt and Reed Laird, of the Department of Metallurgy. The results are shown in Figs. 2 to 5 and beneath each radiograph is shown the fractured weld, after the films had been removed. It was necessary to saw partly through each weld in order to make it break at that point rather than outside the weld, for most of the welds had been built up to a much thicker section than that of the plates in

[2]Barrett, Gezelius and Mehl. *Metals and Alloys*, Dec. 1930.

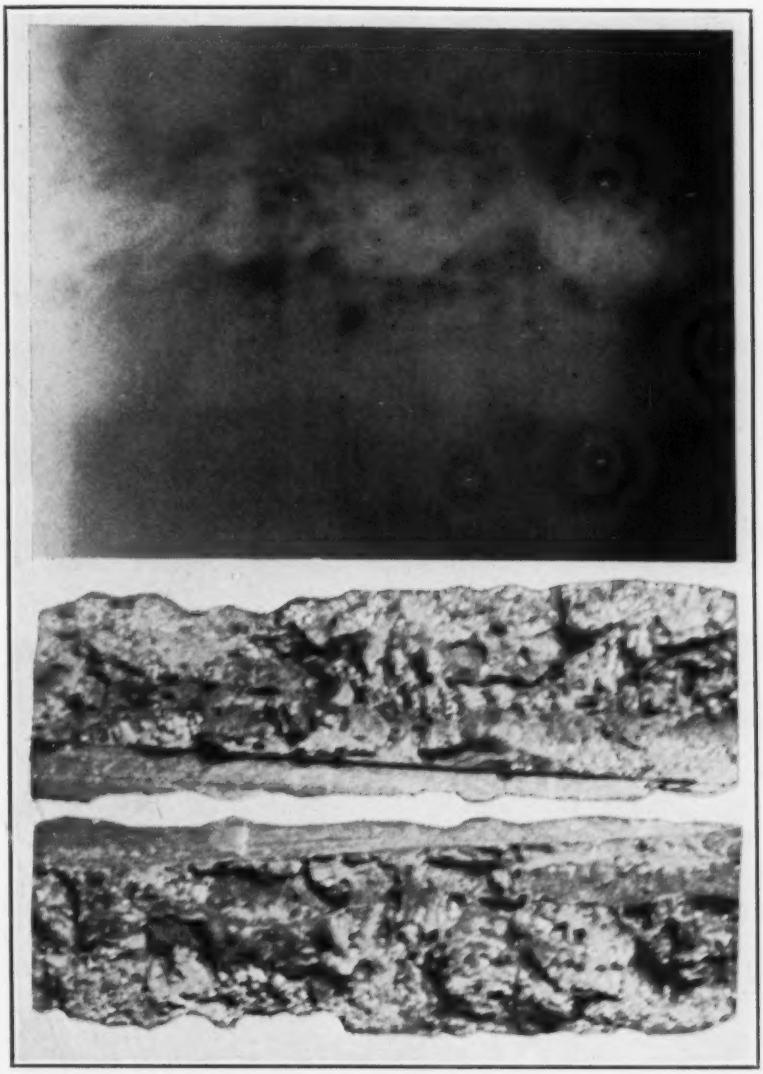

Fig. 2—Gamma-Ray Radiograph of a Defective Weld. The Fracture of the Weld is Shown Below.

which the weld was made. The saw marks are visible in each fracture.

The results show that the makers of the welds possessed surprisingly good control over the process, and were able to make a perfect weld or a very defective weld at will.

Figs. 2 and 3 show the gamma radiographs of two defective welds. Fig. 2 shows an extreme degree of porosity and slag inclusions. The entire weld is honey-combed. Fig. 3 shows lack of complete fusion.

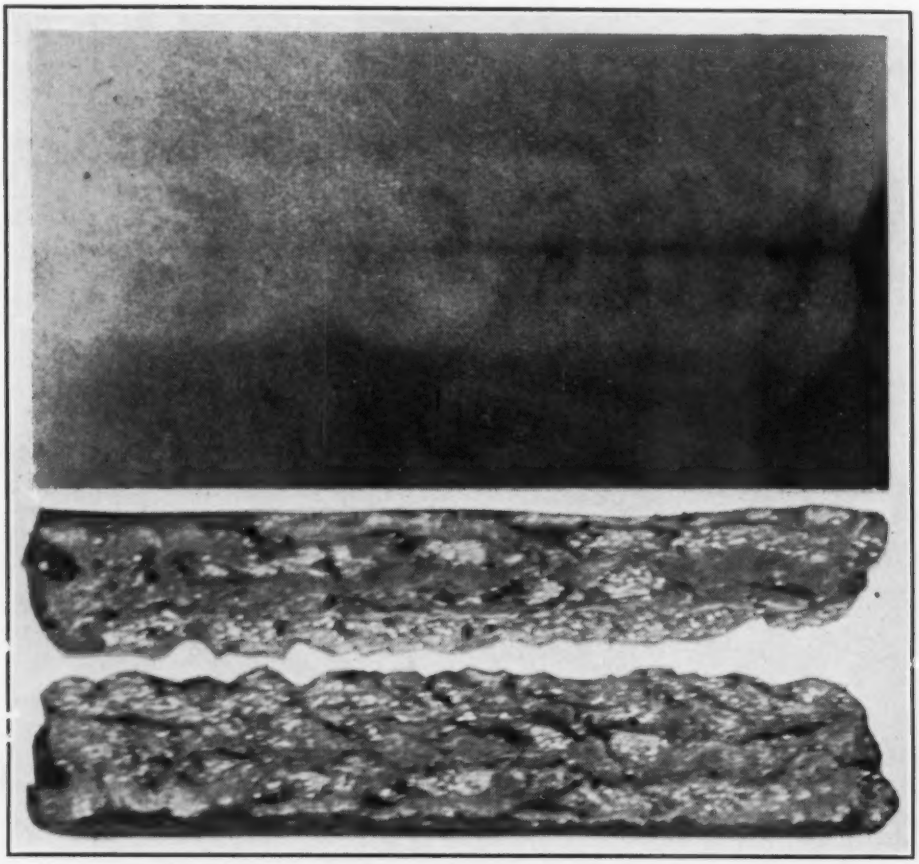

Fig. 3—Gamma-Ray Radiograph of a Defective Weld Showing Considerable Porosity. The Fracture of the Weld is Shown Below.

While the gamma radiographs, like other radiographs, do not reproduce well, still they are comparatively easy to interpret as compared with the fracture reproductions. The fractures lose intelligibility due to absence of color in the reproductions. Thus the blue color of a hot shrinkage crack, or the brightness of a gas pocket, as compared with the dull appearance of a slag inclusion, are not distinguishable in the photographs of the fractures.

Figs. 4 and 5 show the gamma radiographs and fractures of the two sound welds. It is just as important that the method of inspection shall show no indication of defects which are, in fact, not present, as it is for the method to reveal defects in unsound welds.

Discussion of Results

Of the 10 welds tested (four of which are shown in Figs.

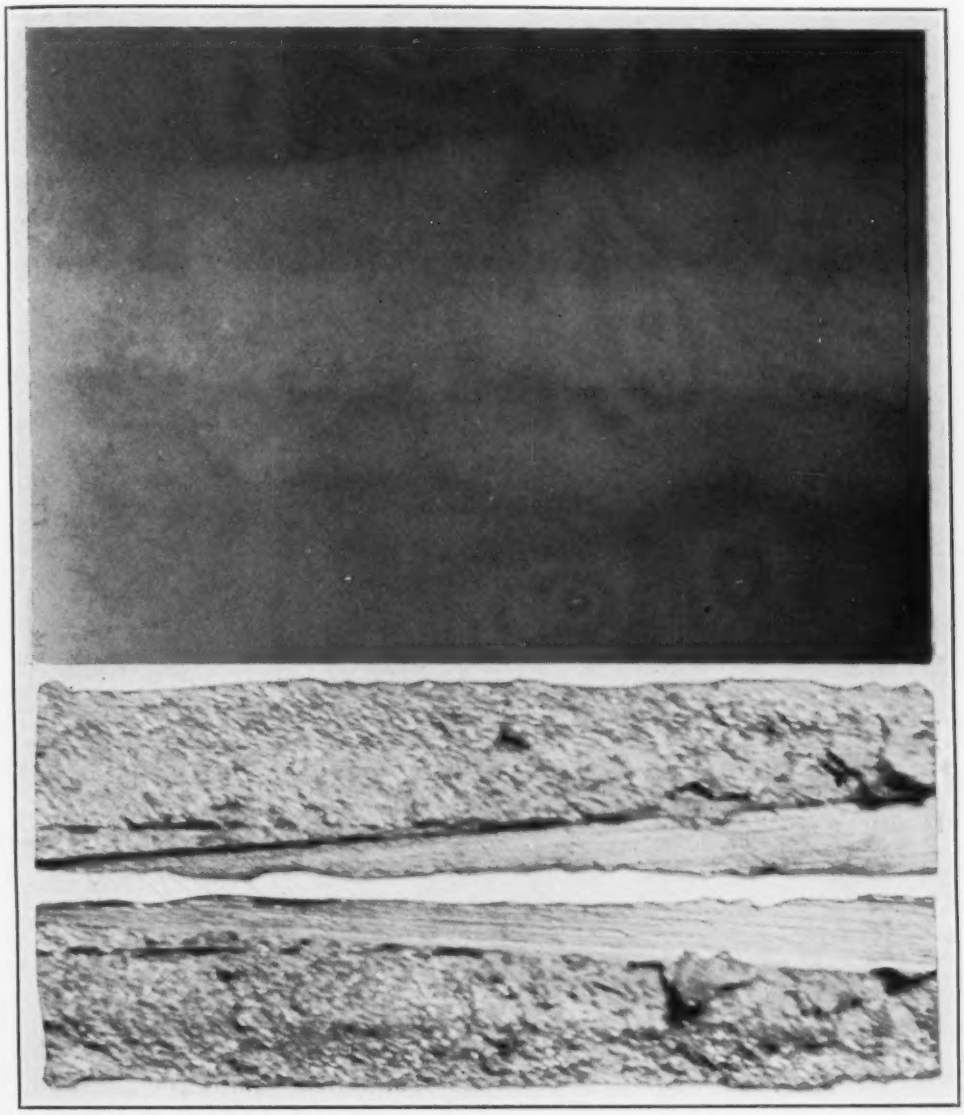

Fig. 4—Gamma-Ray Radiograph of a Sound Weld. The Fracture of the Weld is Shown Below.

2 to 5) the gamma-ray method made it possible to pick out the five defective ones without error, and showed the five sound ones as such. The degree of definition and the sensitivity of the method seem to be adequate to reveal the flaws which are present in improperly made welds of this kind. It is important in examining welds that the distance from source of radiation to weld be as great as the strength of the source and the time available will permit, as was done in this case.

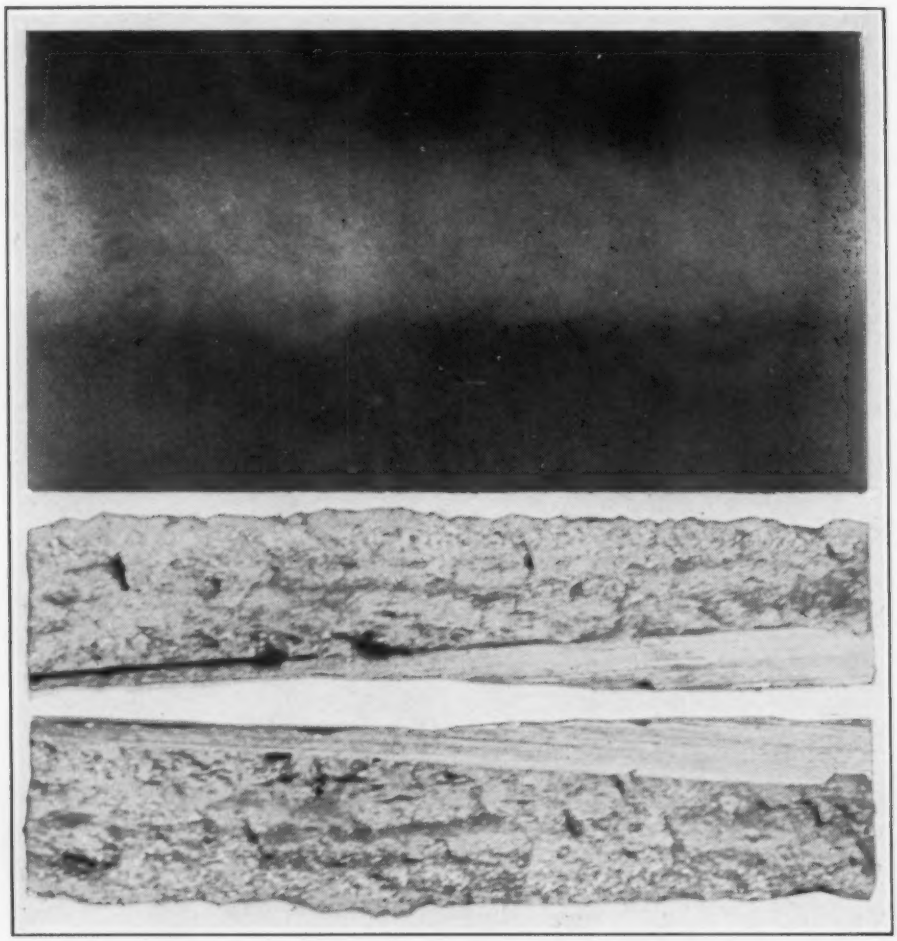

Fig. 5—Gamma-Ray Radiograph of a Sound Weld. The Fracture of the Weld is Shown Below.

Acknowledgments

The author takes this opportunity to express his appreciation of the courtesy of the Babcock and Wilcox Co., the Westinghouse Electric and Mfg. Co., the Una Welding and Bonding Co., the Wilson Welder and Metals Co., and the Lincoln Electric Co. for supplying specimens; to the Radon Co. for the loan of the radium; to Messrs. Hewitt and Laird for assistance in the exposures; to Dr. R. F. Mehl and his staff at the Naval Research Laboratory for reproducing the radiographs, and to Professor Bradley Stoughton, Director of Metallurgical Engineering at Lehigh University, for his encouragement and guidance.

DISCUSSION

Written Discussion: By Herbert R. Isenburger, Secy.-Treas. St. John X-Ray Service Corporation, 505 Fifth Avenue, New York City.

We have used and are using both these methods (X-rays and gamma rays) to great advantage in particular cases and have been impartial observers to their respective merits. It is our opinion that gamma-ray inspection does not lend itself advantageously to the examination of welded test plates. Nothing in Dr. Doan's paper leads us to change our opinion.

As Dr. Doan mentioned, the tests described in his paper have been made during the Welding Symposium at Lehigh University on the 27th of March, 1931. At that time Dr. Doan read a paper on this same subject to which I submitted a written discussion. I also had the opportunity after the sessions to discuss our problems with Dr. Doan. At that time I expressed the wish to see some practical results, especially on welds in 3-inch and heavier plate stock. I had hoped that in his new paper Dr. Doan would tell us something of his experiences in practice. Unfortunately, this is not the case. The results shown by Dr. Doan strongly indicate that gamma-ray inspection of welds 1 inch thick and less is not advisable.

The purpose of radiographic examination is to study the interior conditions of the weld and possibly to draw conclusions from these conditions which will modify or correct the welding technique. Radiographic examination may be applied to the training of welders, to develop proper welding procedure, to check up on technique during production, and so on. It has been our experience in routine inspection of welded test plates that X-rays will do the job perfectly, since this method is quick, reliable and economical.

All these applications just mentioned need as accurate results as possible, giving as much detail of the interior conditions as can be obtained. As Dr. Doan states, the bad welds have been made purposely as poor as possible. I fully agree with him that such material will never be found in ordinary construction. We, therefore, cannot see the value of using such—to say the least—unusual conditions as examples for the appearance of the most important defects. Besides, the pictures only show how poorly even the most exaggerated defects will show up in a radiograph.

Dr. Doan states that he used 1/20 gram of radium and exposed the test plates for 18 hours. One gram would have reduced the exposure time to less than an hour, he states. The secret of getting good results in radiography is the focal spot. We want to use as fine a focus as possible in order to obtain sharply defined outlines. In X-ray inspection we are using a point like source, whereas in gamma-ray inspection we have to use an elongated capsule. Naturally, the larger the amount of radium the bigger this container. We, therefore, are bound to obtain a much less intense image with a large amount of radium than we would with a smaller quantity. This means for Dr. Doan's tests that his set-up was as ideal for gamma-ray inspection as it could have been. Any larger amount of radium would have given him much less detail in the pictures than he obtained, and even these we consider unsuitable. But I am sure that with one gram of radium we would not have been able to obtain any results, due to the very broad focal spot.

With each of his illustrations Dr. Doan shows a photograph of the fracture of the weld. I think that these photographs do not help toward understanding the meaning of the radiographs, in some cases they may even be misleading.

If lack of fusion exists in a weld, it would usually occur in such fine cracks —unless it is accompanied by slag inclusions—that it requires the best technique to detect it even with the much more sensitive X-ray method. We herewith attach an X-ray photograph, in Fig. 1, of a double "V" weld in ¾-inch plate.

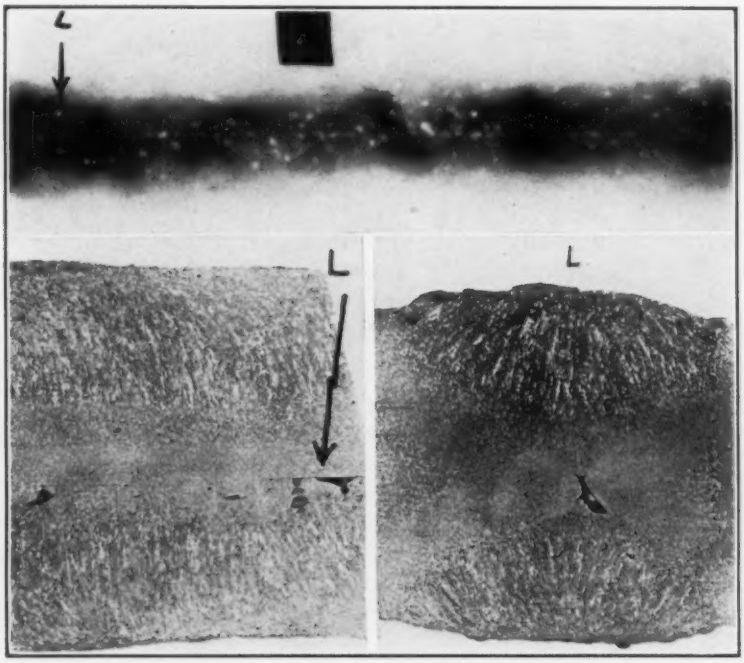

Fig. 1—Double V Weld on ¾-Inch Plate.

This shows lack of fusion through the root of the weld and general porosity. A cross-section at "L" is shown in the macrograph at the lower right and a length section of the same portion at the left in 3 times magnification. After having seen Dr. Doan's results, we are certain that these severe conditions would not have been disclosed in a radiograph.

Having had considerable experience with both gamma and X-rays and after having seen these negative results, we must say that the gamma-ray method is not sensitive enough and not fast enough for the examination of test plates where we want to get an immediate answer with very accurate and reliable results, not to speak of the great expense which is quite inappropriate for this purpose. We would have liked to have heard something from Dr. Doan about the economical aspects of his method.

Our own experience with gamma-ray inspection lies primarily in the field of steel castings. There are distinct advantages for this method especially on thicknesses above 3 inches of steel. We could see similar uses for weld inspection; for instance, to examine the circumferential seams of pressure

vessels. It would not be economical on longitudinal seams. Radium cannot be used for the inspection of welded boilers which fall under the latest A.S.M.E. Code requirements, since with this method we will not find defects "of a thickness 2 per cent of the base plate"; about 3 per cent is the limit. For most of the other welded constructions which should be inspected, gamma-rays would be much too slow.

Besides the very great cost of radium, it is dangerous to handle this material continuously, since even with the greatest precautions one will be exposed to the rays which in time accumulate in the body. Dr. Doan raises

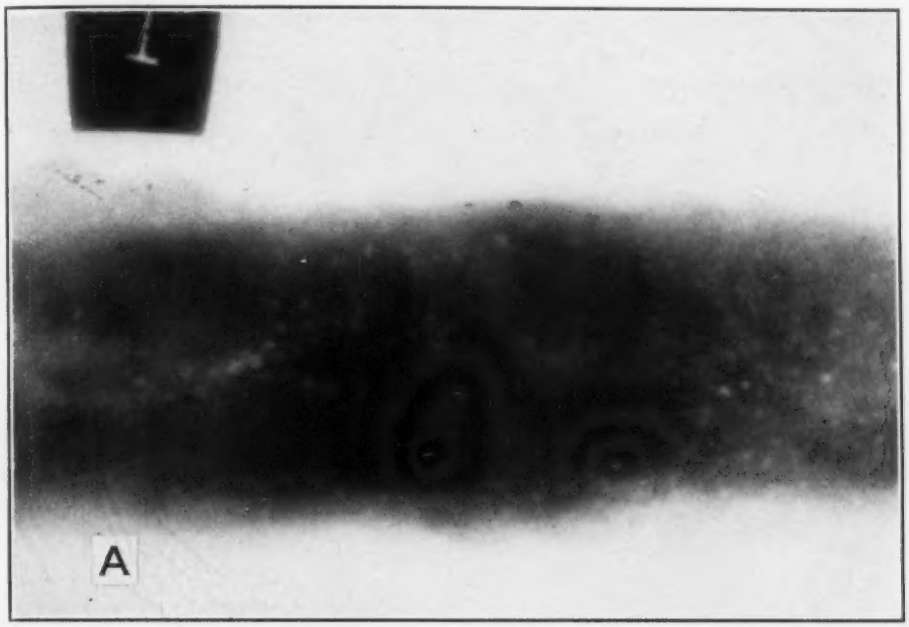

Fig. 2A—X-ray Photograph Through a Very Porous Weld.

the question of the necessity of precaution, but nowhere in the article is this question discussed. We do not know of any sufficient precaution to protect the operator against final injuries.

In answer to his question, "Will the gamma-ray method reveal these flaws?" we should say: In most cases where we want to use gamma rays they will not be sensitive enough to distinguish between the various defects. In answer to his question, "How clearly will they be observed?" we should say: Defects can be observed if larger than about 3 per cent of the total thickness of the material, if the steel is more than 3 inches thick.

In the matter of inspecting welds with the gamma-ray method all of his questions will have to be answered negatively. There may, however, be a field for radium inspection of welded structures for heavier thicknesses than commercially available X-ray apparatus can penetrate in a reasonable exposure time, or it may be used for field inspection, where it would be easier to bring a small capsule of radium to the job than to set up X-ray equipment. We

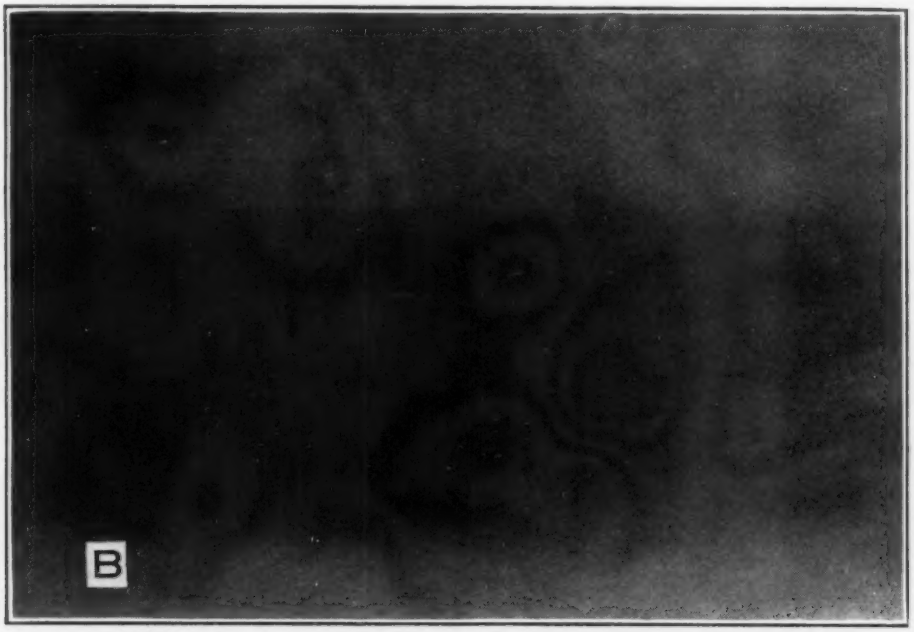

Fig. 2B—Radiograph of the Same Weld Made with a Large Amount of Radium.

Fig. 2C—Radiograph Made with Small Amount of Radium Using Longer Exposure.

would like to hear from Dr. Doan whether such work has been done and with what results.

In order to confirm our conclusion, we have made the following test: A fusion welded test plate ¾-inch thick was X-rayed, using a suitable exposure technique to obtain a picture in one minute. Fig. 2A shows this X-ray which is a little overexposed, but still you can observe numerous small spots within the weld zone which indicate a general bad porosity. There are also some fine cracks visible on the negative; unfortunately these details have been lost in reproduction.

We then made two radiographs, using the same exposure technique as before, but changed the time of exposure so that we expected to obtain a good penetration. That we did get this penetration can be seen by the image of a little lead marker which shows up in each case.

The radiograph Fig. 2-B was made under conditions similar to those Dr. Doan used for his tests. We exposed the plate for 11 hours to the radiation of 10 milligrams of radium. You can clearly notice the number 1, but you are not able to determine from this picture that it was made of a very porous weld. In fact any expert would pass such a radiograph as of sound material.

The second radiograph Fig. 2-C was obtained from 335 milligrams of radium in a 20-minute exposure. The diffused image of the number illustrates the previous statement that the broader the focal spot the less sharpness of the details will be obtained. Although we get more penetration here than in the first radiograph, the defects present in the weld cannot be observed.

Before starting the radium tests we fastened a punched sheet of steel representing 2.5 per cent of the thickness of the plate alongside the weld. In none of the radiographs this marker can be observed. We would like to know from Dr. Doan how he determined his 2 per cent factor in the test described.

Concluding our discussion as to the practical aspects of gamma-ray inspection of welds, we rather doubt whether they can be employed for this purpose. Our test indicates that we will not be able to obtain the actual conditions of the inside of the metal. And if we get any of the defects they certainly are greater than 3 per cent of the total thickness. This means that we will not be able to detect lack of fusion which is the most important defect we want to find. And since a doubtful nondestructive test is worse than none at all, we would not recommend radium inspection of welds thinner than 3 inches.

Written Discussion: By J. C. Lincoln, president, The Lincoln Electric Company, Cleveland.

This paper by Dr. Doan opens up the whole subject of inspection by photographs of the weld metal.

The most disturbing factor in connection with this is the fact that all that the photograph shows is the relative amount of metal in each part of the weld. The variation in density shows on the plate as the variation in density of light photographed. The unfortunate situation is that a surface imperfection will make just as much variation in the photograph as an imperfection under the surface. While surface imperfection may have nothing to do with the strength of the weld, it will show as an imperfection just as much as a hole in the weld metal, which would weaken it materially. Therefore, if any photographic means is used for determining the strength of weld certainly the photographs of the upper and lower surface should also be shown

with the X-ray or gamma-ray photograph. The results cannot be judged without it.

Sometime the general public will appreciate the fact that welding has advanced to the point where the necessity for these precautions has long since passed.

We buy steel, which has a certain number of imperfections, and use it without photographing each piece, and yet the chances for imperfections in the steel are certainly as great as the chances for imperfections in the weld if standard methods are used.

We still trust our lives to castings without photographing them in spite of the fact that imperfections are much more probable than would be the case in welds made under proper procedure control. We trust our lives to concrete where the possibility for imperfection is enormously greater than in any of the cases cited above. The only reason we question the weld is because of its newness, and newness is something which will be cured by time.

Written Discussion: By James W. Owens, director of engineering, Welding Engineering and Research Corporation, New York City.

I have read with interest Dr. Doan's paper, and prior to the meeting had the opportunity of not only reading over the discussion of Mr. Isenburger but collaborating with him on an investigation to determine the correctness of his conclusions that the gamma ray is not suitable for detecting small defects as found in welds.

An examination of the "sound weld" shown in Figs. 4 and 5 of Dr. Doan's paper would apparently verify these conclusions, for the fracture shows defects in the welds which are not indicated in the radiographs, although the depth of these defects appears to be greater than 2 per cent of the plate thickness, or the limit set by Dr. Doan.

The fracturing of a weld longitudinally through its center does not give any information on the most serious and likely defect to be found in a welded joint, viz., a lack of fusion of the base metal with the weld metal, and materially restricts the examination within a very narrow plane.

Mr. Isenburger's examinations of the welded plate furnished by us for this purpose and wherein he used both the X-ray and the gamma ray, seem to confirm his conclusions as to relative effectiveness of the two methods in determining the soundness of a weld. The X-ray photograph indicates a considerable amount of porosity, whereas the radiographs are free from porosity and from their general appearance one would conclude that the weld was sound.

Of course, even admitting that the gamma ray has its limitations, nevertheless its portability feature gives it a field of usefulness not possessed by the X-ray and under certain conditions, particularly where large defects are to be expected and avoided as in heavy castings, it would be of such an advantage that its shortcomings, insofar as the detection of small defects is concerned, could be overlooked, i.e., provided other shortcomings mentioned by Mr. Isenburger would not prohibit its use.

H. R. ISENBURGER: I would like to add a few words to the remarks Dr. Doan made just now but which were not preprinted. He stated that the container in which the radium is carried around weighs just a few pounds. It

is necessary to use at least 2 inches of lead in order to protect yourselves against the gamma radiation. One per cent of the gamma rays will come through 2 inches, and such a container may weigh about 50 pounds. I handle radium and I always have to take a car if I want to carry that around.

Another statement Dr. Doan made was that X-ray equipment was only used in the laboratory. We have been doing this kind of work for years and we have sent around our X-ray equipment, in one case to a factory where they fabricated pipe, and had a furnace right next to the place where we set up the equipment. Frequently, X-ray equipment is used in the boiler shop now since the new boiler code requirements call for X-ray inspection of welded pressure vessels.

I just wanted to correct Dr. Doan in those statements.

WILLAM D. HALSEY:[1] I have not seen this paper before. I have only had an opportunity to read it over since I came in the room, and perhaps my reading is not very good but I have not found in it just what thickness of plate these specimens were. It would be interesting to know that. In Fig. 2 there is shown the gamma-ray picture of the weld and the fracture specimen. While I believe that it would be admitted by anybody who is at all acquainted with either gamma-ray or X-ray examination of weld, that that weld is one which you would not consider a good one, at the same time I would expect to find a much greater degree of defect shown on the gamma-ray film than is indicated here. That looks to be in the fractured specimen quite a defective weld. To my mind it does not match up, as I would expect it to match up, in the gamma-ray film. On the specimens shown in Figs. 4 and 5, they have been broken apparently through the middle of the weld. I agree with Mr. Isenburger that it would have been interesting if X-ray pictures had been made of those same welds. In the insurance business we are particularly interested in knowing if we are getting a sound weld. One of the defects that we are finding more or less common is the slag inclusion on the side wall. Are we certain that in these particular welds we do not have slag inclusion on the side wall? A comparison would have been valuable in that respect.

DR. G. M. ENOS:[2] I would like to ask Dr. Doan if any macroscopic or microscopic studies were made of the sections to supplement the work of the gamma rays. If the X-rays were not used, perhaps the microscopic studies might have been helpful.

Author's Closure

I suppose the development of a new method always arouses certain doubts in the mind of those interested in the older methods, and I think these doubts when freely expressed are of real assistance in the conservative growth of the new development. I must point out again, I think, that each method, the old and the new, has specific advantages for meeting certain conditions and without a doubt both will continue to be used. It is quite true that the advantage of thickness, in which the gamma-ray method will show the great-

[1]Hartford Steam Boiler Inspection and Insurance Co., Hartford, Conn.

[2]Professor of metallurgy, University of Cincinnati.

est advantage over X-ray, is in that thickness above 3 inches. I think results from the testing of welds 3 inches thick and thicker will soon be available. In regard to the question about the sensitivity of the method and how that was determined, a paper covering this phase and published in the December issue of *Metals and Alloys,* in 1930, should be consulted. The sensitivity was determined by milling slots of different thicknesses in a piece of boiler plate, enclosing that plate in a pile of similar plates, and finding out after exposure of the whole pile of plates what was the smallest slot that would register on the film. This paper gives exact quantitative data.

As to the tests of a weld which Mr. Isenburger made with X-rays and then repeated with gamma rays, I would not attempt to criticize his methods of using gamma rays, knowing, as I do, so little about the exact procedure which he followed in using them.

The question of risk, I think, is important, because it occurs to one's mind at once, and I want to repeat at this time that the examination of materials by gamma rays does not involve any danger to the operator if he is content to use the devices recommended for his use.

This is an important statement and is based on personal experience as well as published authority. I think we must keep that clearly in mind. It is quite possible to be careless with radium, as with anything else, any other powerful tool, but if the prescribed precautions are followed, there is no necessary exposure or risk involved.

In reply to Mr. Lincoln, I entirely agree that a surface inspection should always accompany radiography. It is scarcely conceivable that visual inspection of the exterior would be omitted if one is sufficiently interested to examine the interior of the weld. It will not always be desirable or necessary, however, to record the surface appearance photographically.

The thickness of the plates should have been given. They were half inch plates, with the exception of one shown in Fig. 2, the porous one, which was ⅝ inch. The thickness of the welds is given in the paper.

Mr. Owens points out that lack of fusion in a weld would not be shown by a fracture of the weld. One of the five "bad" test specimens in which lack of fusion existed "fractured" in such a way that the original machined surface of the scarf was exposed. We did not confine the fracture strictly to the center of the weld.

What is important in this connection, however, is the fact that a weld in which lack of fusion is the only defect, that is, one in which the weld metal fits the "V" as if machined to size, but is otherwise entirely homogeneous and sound, would in any kind of radiographic test, if made horizontally, appear sound. Fortunately, lack of fusion is usually, if not always, accompanied by porosity and slag inclusions, which defects do show up readily upon radiography.

Relative to Mr. Owens' estimation at "more than 2 per cent" for the fractures in "good" welds, Figs. 4 and 5, and Mr. Halsey's remarks, I would caution against attempting to estimate so closely from a photograph, especially where the shadows are as deceptive as they are in photographs of rough fractured surfaces. I would prefer to refer their attention to the quantitative tests in *Metals and Alloys* mentioned above.

I agree that it would have been interesting to show X-ray radiographs of the same welds for comparison with gamma rays. I think that would have been valuable, but the purpose of the paper was not to show that one method was better than another, but merely to show the possibility of the gamma-ray method for defects relatively small.

In reply to Dr. Enos, no micrographic or microscopic studies of the welds were made. As far as we know, radiography is not of much help in that respect.

As to the diffraction patterns, the wave length of gamma rays as compared with the interplanar distance in the crystal, that is atomic dimensions, is too small to give any diffraction value.

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